

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 1 163 552 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
**27.08.2003 Bulletin 2003/35**

(51) Int Cl.7: **G03F 1/00, G03F 7/16,  
H05K 3/12, B41M 3/00**

(21) Application number: **00935358.2**

(86) International application number:  
**PCT/GB00/02077**

(22) Date of filing: **30.05.2000**

(87) International publication number:  
**WO 01/011426 (15.02.2001 Gazette 2001/07)**

**(54) METHOD OF FORMING A MASKING PATTERN ON A SURFACE**

VERFAHREN ZUR ERZEUGUNG EINER MASKE AUF EINER OBERFLÄCHE

PROCEDE DE FORMATION D'UN MOTIF DE MASQUAGE SUR UNE SURFACE

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**

(30) Priority: **27.05.1999 GB 9912437  
10.03.2000 GB 0005929**

(43) Date of publication of application:  
**19.12.2001 Bulletin 2001/51**

(73) Proprietors:  
• **Patterning Technologies Limited  
Green Drift, Royston, Herts SG8 5DY (GB)**  
• **Jetmask Limited  
Broxbourne EN10 7BN (GB)**

(72) Inventors:  
• **SPEAKMAN, Stuart  
Chelmsford Essex CM3 3LW (GB)**

• **GARDNER, Ian, Andrew  
Patterning Technologies Ltd.  
Royston, Hertfordshire SG8 5DY (GB)**  
• **BRESLER, Eric Patterning Technologies Ltd.  
Royston, Hertfordshire SG8 5DY (GB)**

(74) Representative: **Cozens, Paul Dennis et al  
Mathys & Squire  
100 Grays Inn Road  
London WC1X 8AL (GB)**

(56) References cited:  
**EP-A- 0 641 648 EP-A- 0 776 763  
EP-A- 1 162 079 DE-A- 4 228 344  
DE-A- 4 329 338 US-A- 3 795 443  
US-A- 4 929 400 US-A- 5 810 988**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**EP 1 163 552 B1**

**Description**

**[0001]** The present invention relates to a method and apparatus for forming a mask pattern on a surface. In one preferred embodiment, the present invention provides a method of drop-on-demand printing of a relief pattern on a surface using computer generated image files (i.e., Gerber input to bitmap output).

**[0002]** In a wide variety of inorganic or organic-based microelectronic and opto-electronic device and circuit manufacturing applications it is necessary to pattern one or more materials that comprise the device or circuit being fabricated. The pattern being formed can be for one of many reasons, including:

- Etch mask (for wet, dry, electrochemical, etc.)
- Selective area deposition mask (lift-off, air-bridge [2-level process], electroplating, electrophoresis, etc.)
- Containment well (for phosphors, liquid crystals, light emitting polymers, etc.)
- Dielectric micro-via promoting multi-level metal interconnections
- Metal conductor cross-over resistor-capacitor nodal network
- 2-D and 3-D membranes (static or removable)
- Piece part interlevel spacer (providing controlled gap dimension between piece parts)
- Piece part reflowable thermosetting adhesive (localised adhesive for bonding pieces parts)

**[0003]** Such patterned features could be removed or left in place after serving the required function.

**[0004]** The most popular method of providing a surface relief structure is photolithography. This requires the use of a photosensitive material that is applied to a surface as a whole area coating (spin-casting or dipping) or as a whole area sheet (lamination). The material is applied in a light controlled laboratory in order to ensure that the photosensitive material is not pre-exposed prior to introducing the required pattern mask in front of the coated wafer. The patterning mask can be either a contact mask, a proximity mask, or a projection mask. In all cases the mask must be manufactured as a discrete unit to a high precision and must be carefully protected against damage or dust/particulate collection. Once the mask is put in place then a lamp, of a radiation matched to the photoinitiator used in the photosensitive material, can be used to expose the substrate coating in those areas not protected by the mask. Depending upon the photosensitive material type employed the pattern transfer achieved can be either positive or negative with respect to the mask. After exposure the photosensitive material must be exposed to a developing chemical that modifies the chemistry of the coating in such a manner as to permit the untreated material to be washed away in a water-based dip bath or conveyor shower/spray.

**[0005]** Although spin-cast, dip, or sheet lamination photolithographic methods of achieving a surface relief pattern are successful they do have a number of problems, namely:

- Material wastage (because whole area technique)
- Selective area 3-D patterning is extremely difficult and time consuming
- Chemistry used in photosensitive material has high toxicity rating
- Disposability of large volumes of toxic and developing chemicals
- Simple pattern is still a multiple step process of

Photoresist coating;  
Mask alignment;  
Radiation exposure;  
Mask removal;  
Pattern development;  
Excess material rinse removal; and  
Substrate drying.

**[0006]** It is possible to address one or more of these problems by introducing further processes that can provide a patterned relief structure on a surface, including stencilling (screen printing), microdot transfer (stamping), and laser writing-etching (includes ablation scribing and direct-write photolithography equivalent imaging). Each technique has its merits and limitations which tend to be driven by the detail of the intended application, namely:

- Speed of pattern generation
- Relief pattern thickness
- Controlled etch capability
- Cost of process
- Ease of use of process

However, not all of the problems cited above can be addressed by any one process.

[0007] The preferred embodiments of the present invention seeks to solve these and other problems.

[0008] EP-A-0 641 648 describes apparatus for direct production of photopolymeric printing plates. The apparatus comprises a rotatable drum for retaining the substrate to be printed, at least one nozzle for ejecting the photopolymeric ink composition, and a UV source located to expose the printed surface of the substrate to UV radiation.

[0009] EP-A-0 776 763 describes a process for the production of lithographic printing plates in which monomers are deposited as droplets from an ink jet printer head in predetermined manner to describe the image pattern and polymerisation is carried out by exposing the plate to electromagnetic radiation.

[0010] EP-A-1 162 079 describes a method for cross-linking photosensitive inks in polymerisable inks by applying ultraviolet radiation only on the inked dots on a base, not on the non-inked surfaces.

[0011] US 4,929,400 describes a method of producing monodisperse microspheres by deploying a liquid monomer droplet into a containerless environment and subjecting the droplet to ultraviolet radiation.

[0012] DE 43 29 338 describes a method for forming a photoresist pattern which includes a step of injecting droplets during which an injection head is driven in accordance with a drive signal to inject solution droplets of a photoresist solution onto a base part. A curing step cures the solution droplets which have been injected onto the base part, an etching step etches the base part and a photoresist removal step removes a photoresist pattern.

[0013] In one aspect, the present invention provides a method of forming a masking pattern on a surface, said method comprising the steps of:

using the technique of drop-on-demand printing to deposit from droplet deposition apparatus a plurality of droplets on to a surface to form a masking pattern, said droplets passing through an operating zone located between the deposition apparatus and the surface; and  
locally exposing the operating zone to electromagnetic radiation so as to control coalescence of droplets on the surface, thereby controlling the solidity of the masking pattern.

[0014] As discussed in more detail below, control of the local environment only of the operating zone has been found to have a significant influence on the formation of the masking pattern on the surface. Preferably, formation of the masking pattern is controlled so that the masking pattern has predetermined structural properties.

[0015] In drop-on-demand printing, individual droplets, or a continuous stream of droplets, are deposited on the surface to form the masking pattern. Examples of drop-on-demand printing include ink jet methods based on piezoelectric, piezo resistive, relaxor and bubble-jet induced pressure generation for ejecting a droplet from a printhead.

[0016] The masking pattern can be formed from a wide variety of different materials, depending on the purpose of the masking pattern. For example, the pattern may be formed from at least one of an alkyd, acrylic, phenolic, chlorinated rubber, epoxy, polyester, polyurethane, polyvinyl, silicone, fluorocarbon, polyimide, polyamide, and polystyrene. The pattern may be formed from one of metallic, dielectric, magnetic, light emitting, light absorbing, light transmitting, conducting, insulating, semiconducting or superconducting material. The deposition material may be 100% solid polymer.

[0017] The deposition material may be an organically modified ceramic.

[0018] The deposition material may be in the form of a solution, or solution-gelation. The solvent may be one of water, a lower alcohol, ethylene glycol, acetone, hexane, benzene, chlorobenzene, toluene, para-xylene and methylene chloride.

[0019] Preferably, the operating zone extends from the deposition apparatus to the surface. However, the operating zone may extend only partially between the deposition apparatus and the surface.

[0020] In a preferred embodiment, relative movement is effected between the deposition apparatus and the surface so as to move said operating zone across the surface during formation of the masking pattern.

[0021] Preferably, the local environment of the operating zone is controlled for one or more of at least the following reasons:

- (i) so as to control the coalescence of the droplets on the surface;
- (ii) so as to control the spreading of the droplets on the surface;
- (iii) so as to control placement of the droplets on the surface; and
- (iv) so as to avoid contamination of the droplets.

[0022] Preferably, the local temperature of the operating zone is controlled so as to control the rate of solidification of the droplets on the surface.

[0023] Preferably, the local atmosphere of the operating zone is controlled. Such localised atmosphere control can provide a much cheaper means of controlling the required deposition characteristics as opposed to atmosphere control associated with the whole area to be printed on. This zone can in one embodiment be achieved by surrounding the printhead with a containment surface, such as, for example, a bellows-type structure that provides a positive pressure of

air or a specified inert or reactive gas injection (gas being heated or cooled). A soft vacuum can also be supported within the bellows, making use of a dry vacuum pumping arrangement.

**[0024]** Thus, in one preferred arrangement an at least partial vacuum is generated in the operating zone so as to substantially avoid contamination of the droplets during passage from the deposition apparatus to the surface. A pressure differential extending between the deposition apparatus and the surface may be established in the operating zone. Alternatively, or additionally, an inert or reactive gas may be introduced into the operating zone during droplet deposition.

**[0025]** In a preferred embodiment the operating zone is locally exposed to electromagnetic radiation so as to control coalescence of droplets on the surface, thereby controlling the solidity of the masking pattern. The duration of the local exposure of the operating zone to electromagnetic radiation may be controlled so as to control the spreading of the droplets on the surface, thereby controlling the resultant shape of the masking pattern. Alternatively, or additionally, the intensity of electromagnetic radiation is controlled so as to control the spreading of the droplets on the surface, thereby controlling the resultant shape of the masking pattern.

**[0026]** The droplets of deposition material may be radiation cured prior to and/or after deposition on the surface. In one embodiment, the radiation curing has a threshold energy of  $\geq 1 \text{ mJ} \cdot \text{cm}^{-2}$ .

**[0027]** For instance, linewidth and profile control of the masking pattern may be achieved by controlling the time after impact that the deposited material is exposed to the radiation curing. The time period is preferably in the range from 1 to 2000 ms, more preferably in the range from 50 to 300 ms.

**[0028]** Exposure to a critical radiation has been found to promote a change in the liquid material rheology thereby affecting the rate of spreading of a droplet over the surface and the rate and degree of coalescence with adjacent droplets. Such control of the droplet coalescence and curing can enable a straight-edged, parallel-sided masking pattern to be formed in a time domain from 0 to 100 milliseconds after droplet deposition. Computational fluid dynamic (CFD) modelling has provided evidence for the impact dynamics and surface wetting behaviour of droplets in the time domain up to and during coalescence. The droplet volume, diameter, and impact energy, coupled with the droplet ejection time (hence impact spacing) have been found to contribute directly to the coalescence behaviour.

**[0029]** The specifics of the use of the masking pattern dictate the rate of droplet ejection and the rate of surface transfer leading to a droplet centre-to-centre spacing. Adjustments to the operating parameters can permit direct control of the droplet-to-droplet coalescence time domain.

**[0030]** To achieve a dynamic range in linewidth, the surface wetting and rate of solidification of a droplet on the surface are preferably controlled. This may be achieved by controlling the surface energy of the surface and the properties of the material used in the deposition process. The surface energy control can be affected by many methods including abrasion, polishing, ozone treatment, plasma exposure, and coating with a non-wetting material. The fluid solidification control can be achieved by chemical design of the fluid and by the type, degree, and timing of the radiation curing.

**[0031]** The radiation curing can be provided by any suitable means.

**[0032]** To provide the ability to select the time and location relative to the droplet impact zone when the radiation is allowed to interact with the deposited feature, the light output from a radiation source may be transferred to the printhead using a fibre-optic light-pipe arrangement. Multiple fibre-optic light-pipes can be employed that are either bundled together or are combined in a unit that provides a line output conversion.

**[0033]** The electromagnetic radiation may be one of ultra violet, Visible, Infrared radiation, Microwaves, and  $\alpha$ -particles). In order to achieve high speed curing it is preferred that both the photoinitiator chemistry of the deposition material and the incident irradiation intensity of the radiation source used to cure the material are controlled, together with the time of exposure to the radiation. The radiation curing may be provided in multiple-wavelengths of radiation co-incident sequentially or in parallel on the deposited droplets.

**[0034]** The radiation source may comprise at least one light emitting diode (LED). The or each LED may be inorganic or organic, and may be based on SiC, InGaN or a PPV derivative. The radiation source may comprise a set of discrete LEDs. Such a source can comprise a number of discrete LEDs that are butted together to form an independently addressable linear or area array of LEDs. Plastic encapsulating packaging can be removed to reduce the bulk of the array to facilitate closer integration to the deposition printhead.

**[0035]** Alternatively, the radiation source may comprise at least one semiconductor quantum-well solid state laser. The or each laser may be inorganic or organic, and may be based on SiC, InGaN or a PPV derivative. The radiation source may comprise a set of discrete lasers. Such a source may comprise an independently addressable array of semiconductor quantum-well stack solid-state lasers. The lasers may be manufactured on a single crystal wafer. The wafer can be diced to produce a line of lasers which can be directly bonded to the printhead or to an angular rotatable housing to facilitate curing of the droplet in-flight, on impact, and on spreading over the surface. Alternatively, the lasers may be manufactured on a flexible plastic sheet.

**[0036]** The radiation source may comprise at least one light emitting polymer (LEP), which may be employed in a strip light or a whole area illumination device. The LEP may be a thin film device. The radiation curing can be achieved as a large area process by making use of thin film inorganic or organic light emitting materials. The thin film device

design defines the wavelength band that will be emitted by the device. The emission can be tuned to suit a specific wavelength or wavelengths. Discrete stripes or bands of wavelength can be achieved in the device manufacture. Stripe or band focusing or defocusing can be achieved with a lenticular lens arrangement. The lenticular lens can also be deposited using drop-on-demand techniques. In one preferred embodiment, the LEP emits a white light which is filtered to select a wavelength for curing or illumination of the deposited masking pattern.

[0037] The present invention can provide a high throughput etch mask printing system by utilising reel-to-reel and/or robotic substrate transfer methods. For example, multiple sets of printheads may be used so as to permit a multiplicity of discrete work stations to be operational along the open length of plastic sheeting retained between the two tensioned "feed" and "accept" drums. Each printhead may deposit the same or respective different deposition materials.

[0038] Preferably, fiducial alignment marks are generated. Serialising coding may be deposited on individual substrates (for example, for printed circuit boards for wet etching). This can be achieved by using drop-on-demand printing methods using coloured or transparent inks.

[0039] The present invention may utilise dynamic imaging of the deposited masking pattern. Such imaging may be provided by a linear imaging device integrated directly on to the printhead. The real-time imaging can be achieved by integrating an imaging array, such as a charge-coupled device (CCD) onto both sides of the printhead assembly, thereby permitting bi-directional print imaging. The real-time imaging can be achieved using inorganic imaging devices such as CCD's or silicon x-y addressable photodiode array's or by thin film organic photoconductive pixel array's (photodiodes).

[0040] In order to enhance processing yield, pattern recognition and software-based overlay comparison may be employed, for example, using a large area organic photoconductive array. This can enable a complete substrate to be imaged at one time without recourse to expensive lens arrangements. The organic photodiode area array preferably has a pixel resolution compatible with the finest feature size to be imaged. The image is preferably on a 1:1 correspondence, making the software-based pattern recognition easier and faster.

[0041] The present invention preferably employs a bimorph or other electronically driven electromagnetic radiation shutter for selectively covering the nozzle aperture of the printhead. The shutter assembly is a micromachined structure. The shutter comprises means for cleaning the nozzle surface. Thus, in another aspect the present invention provides droplet deposition apparatus comprising a deposition chamber, a nozzle in fluid communication with the deposition chamber and a nozzle shutter for selectively covering the nozzle aperture, the shutter including means for cleaning the surface of the nozzle.

[0042] In one preferred embodiment, the cleaning means comprises a set of thin/thick film wiper blades for cleaning the nozzle surface. The apparatus may also comprise a set of fluid ducts to assist the flow of residual ink from the wiper blades to a catchment reservoir located at either end of the shutter assembly. A vacuum suction tube may be located in the reservoir to periodically empty the retained fluid/ink.

[0043] The in-situ environmental and radiation shutter assembly can also act as a real-time pulsed plasma electrode that provides surface pre-treatment adjacent to droplet landing zone and/or as a printhead vacuum priming unit.

[0044] The surface of the wiper blade can be locally hardened to provide an improved cleaning action and wear resistance. The blade is preferably hardened by exposing the surface of the shutter to a beam of high energy ions (ion implantation or plasma immersion implantation).

[0045] The method may employ a number of droplet firing waveforms and sequences, catering for variable speed radiation curing printing. Specific drive waveform sequences can be used depending on the type of masking pattern.

[0046] A surface pre-treatment may be performed, for example, in-situ and/or prior to deposition of the masking pattern. The surface pre-treatment may be performed by a localised ozone, radiation exposure, acidic or alkali jetting from a spray head or an ink jet printhead, or solvent dispensing from a spray head or an ink jet printhead, including a means of drying.

[0047] Real-time height positioning of an ink jet printhead may be performed during the deposition of the masking layer. This positioning may be performed using a bimorph or cantilever-type or servo-drive positioning transducer that permits printhead movement in the z-axis. Height adjustment is preferably in the range from 50 to 2000 microns, more preferably in the range from 0.75 to 1.25 mm. Positioning transducers may be positioned at either end of printhead in order to ensure parallel displacement of the printhead. Such real-time positioning may be a direct result of feedback signal from electro-optical (laser [range finder principle] or LED in conjunction with a phototransistor or photocell pair) or capacitive, or inductive sensing element. Such height control can facilitate direct fluid contact transfer.

[0048] The present invention can enable wide format printing by utilising a printhead enclosure that can house a multiple of printheads. For example, a series of printheads may be butted together with a common nozzle format. This can ensure that although the number of nozzles is increased the resultant parallel-sided pattern is not affected. The butting error could compromise such print, hence the need to integrate a common nozzle plate. The butted printhead may be aligned in the x-y-z axes by utilising piezoelectric positioning of a He-Ne sighting laser assembly that can be removed once the alignment has been completed.

[0049] In order to optimise the mask pattern linewidth, the formulation of the deposition material may be controlled.

Properties of the deposition material, such as the glass transition temperature,  $T_g$ , can affect the hardness and temperature stability of the deposition material. Changes in the bulk-to-surface photoinitiator ratio can also affect the rate of curing. Optimum operation occurs for the range 1: to 4:1 (surface:bulk).

**[0050]** A close-coupled, low temperature, microwave initiated gaseous discharge radiation source may be used to promote large area polymer cross-linking. Lower surface has had fabricated in it a surface relief pattern that permits the discharge induced photo species to couple-out on to the substrate surface and thereby irradiate the mask material. The surface relief required to extract the plasma discharge photons of the desired wavelength (gas specific) can be a dispersion structure such as diffuser, dot matrix, or moth-eyed lens matrix. A preferred embodiment makes use of lenticular lens type array, where the nearly rectangular cross-sectioned (variable angled wall geometry of angle  $\leq 90^\circ$ ) projection width, height, and wall slope affect the efficiency of coupling for the wavelength of light specified.

**[0051]** A specified nozzle plate geometry may be used to affect the placement control of the drops ejected from the nozzle array. If shearing action is employed (i.e., Xaar XJ series printhead) then a nozzle stagger is preferably defined in the nozzle plate to permit straight text printing. In order to obtain a coalescence of drops, leading to a well defined line, it is necessary to vary the drop spacing by operating the printhead outside of standard parameter range.

**[0052]** The masking pattern may be an electrode surface solder reflow resistant mask pattern. In this instance the method used to form the solder mask is similar to that used to form the etch mask defined above, with the difference being that the choice of ink formulation must reflect the higher temperature limits applied to the solder dip coating and thermal wave solder reflow processes. Soluble materials that can be used as the solder mask include silicone, polyimide, PTFE, and epoxy.

**[0053]** The masking pattern may be a 3-D etch mask. A number of device fabrication applications require the production of a variable build height or etch depth feature. It is possible to use the droplet deposition process to define such a feature using either multiple droplets solidified at a specific site or multiple passes of a pattern where the pattern being deposited can be different each time.

**[0054]** In one preferred embodiment, the masking pattern is a dry etch resistant, inorganic etch mask. Etch masks may be formed based on inorganic or mixed organic-inorganic fluid systems. In such cases the properties of the fluid and chemical stability with respect to the printhead materials and nozzle non-wetting coating still apply. An organic-inorganic fluid (ormocer - organically modified ceramic, sol-gel, metallo-organic, etc.) can still employ radiation curing, such as UV. The masking pattern may be an electroless or electrolytic plating bath resistant, etch mask pattern. The method of printing is the same as for printed wiring board etch mask printing. The difference is in the choice of materials used and the need to construct a mask pattern that is 3-dimensional in nature. Typical materials include epoxies, polycarbonates, silicone, PTFE, polychlorotrifluoroethylene, polyimide, polyisoprene, and polypropylenepolystyrene, etc.

**[0055]** The masking pattern may be an additive plating etch mask.

**[0056]** The masking pattern may be a high resolution etch mask. High resolution has a different meaning dependent upon the application being served. For the purpose of this disclosure high resolution means a feature size of less than  $10\mu\text{m}$  [microns].

**[0057]** The masking pattern may be an electrically conducting masking layer. Such a masking layer can be left in place after use, as in the seed layer for electroless/electrolytic plating of an electrode pattern. The masking layer can be carbon-based or metal acetate-based (i.e., palladium), in order to effect a specific conductivity and chemical interfacial reaction prior to plating up with the metal of choice.

**[0058]** The masking pattern may be a decorative surface etch mask. The decorative surface may be based on the properties of the ink(s) being used to form the surface relief pattern. Such a system could be used as a security device due to the unique nature of the particulate distribution in the solid that can be imaged and recorded as a secure signature.

**[0059]** The present invention may utilise a UV (or alternate energy/radiation) line source in the deposition of an etch mask pattern. Such a line source can provide a uniform area of radiation (UV-visible-IR-electron) exposure across the width of the selected printhead. The line source construction in one preferred embodiment makes use of a fibre-optic bundle that is fanned-out to give a single line of fibres of individual diameter in the range 0.25 to 1 mm. The line of fibres are in direct contact and are secured to a polyimide sheet backing material that provides some degree of rigidity and ease of handling.

**[0060]** The present invention also extends to a method of forming a circuit pattern on a circuit board using the technique of droplet ejection to deposit droplets of deposition material, said method comprising depositing a plurality of droplets on said circuit board to at least partially fill via holes formed in the circuit board. Such a method can be performed in two different ways, namely a plated hole in-fill or surface tension driven coating.

**[0061]** The in-fill process makes use of a multiplicity of droplets that under the action of capillary forces causes the droplets to fill the via hole. UV curing solidifies the deposited droplets to form a solid plug.

**[0062]** Surface tension driven coating process requires that the drop size be greater than the size of the via hole to be filled.

**[0063]** Preferably, the method includes the step of subsequently at least partially removing the masking pattern. The removal process can be either dry or wet. The dry process makes use of a plasma based on a variety of gas chemistries including argon, oxygen, argon-oxygen mix, CF<sub>4</sub>-oxygen mix, argon-water vapour, etc. (Inert gas rare-earth series; Reactive gas being hydrogenated, oxygenated, chlorinated, fluorinated, etc.). The wet process makes use of both aqueous and non-aqueous solvent systems. Aqueous based chemical etchants are primarily caustic-based [typical process being spray injection via roller feed of 5% NaOH in H<sub>2</sub>O at 30°C]. The non-aqueous solvent used to remove the acrylate mask include:

- Chloroform (dissolution action)
- Dichloromethane (swelling and dissolution action - quick removal)
- Tetrachloromethane (dissolution action)
- Chlorobenzene (swelling action)
- 1,1,2-trichloroethane (dissolution action)
- N-methyl pyrrolidinone [NMP] (swelling action - slow process)

**[0064]** The method may utilize a dual printhead arrangement with a common integrated radiation curing source. This arrangement may have a radiation source located at the outer edges and the centre of the dual back-to-back printhead arrangement. This permits the printhead to print in a bi-directional mode, providing the same degree of radiation exposure irrespective of the forward or reverse direction print.

**[0065]** The masking pattern may be formed based on chemical attachment transfer. Chemical attachment can be through chirality or via a hydrophilic-type reaction on a catalysed surface.

**[0066]** The present invention can be utilised to form a single panel printed wiring board (PWB) back-to-front auto-registered etch mask printing process. The process can make use of two facing printheads or butted linear arrays of printheads, that have been aligned relative to one another using for example a He-Ne laser beam and a silicon diode photodetector.

**[0067]** The masking pattern may be a near vertical-walled mask pattern. Computational fluid dynamic modelling (based on FlowScience Inc., Flow3D modelling software) of ink jet printhead ejected drop interaction with solid surfaces has suggested that it is possible to create a single dot with a sidewall geometry very close to vertical. The drop spacing and the solidification state of the previous drop, coupled with the impact velocity of the drop and the ink viscosity, affect the rate of coalescence to form a line. In order for the line to have a vertical sidewall profile it is essential that the coalescence process occurs in the time it takes for the drop material to spread-out to the width of the solidified drop (i.e., in a time  $\leq 10\mu\text{seconds}$ ).

**[0068]** The masking pattern may be an ion implantation mask. The objective of such a masking material is to shield the surface under the mask from a high energy ion beam. The energy range of interest spans 10 eV to 50 MeV. The masking layer thickness will depend upon the energy of the irradiating beam. For the highest energy the anticipated mask thickness will be  $\leq 10\mu\text{m}$ .

**[0069]** The masking pattern may be a confinement well mask, such as that used in the manufacture of a single or multiple colour light-emitting polymer displays (see Figure 26). Other such display devices that could make use of such a containment well include inorganic lanthanide dyes or organic small molecule dye structures.

**[0070]** Preferred features of the present invention will now be described, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 is a captured image from an animation sequence resulting from a computational fluid dynamic model of the spreading behaviour of a typical masking ink on a surface whose surface energy is equivalent to that observed for a typical printed wiring board material. Note that the droplet spacing, surface energy interaction, and time before exposure to critical threshold radiation energy dictate the line width and edge quality achieved.

Figure 2 [a-b] are captured images from an animation sequence resulting from a computational fluid dynamic model of the interaction of two ink jet droplets in the 2D vertical plane, covering the time interval from impact out to 1millisecond.

Figure 3 is a captured image from an animation sequence resulting from a computational fluid dynamic model of the interaction of two ink jet droplets in the 2D horizontal plane, covering the time interval from impact out to 1millisecond.

Figure 4 is a schematic of a preferred printing system layout showing the substrate transport relative to the printhead.

Figure 5 [a-b] are schematic diagrams showing the relationship of the radiation line source to the printhead.

Figure 6 is a captured image from an animation sequence resulting from a computational fluid dynamic model of the interaction of two ink jet droplets in 3D, covering the time interval from impact out to 250 millisecond.

Figure 7 is a schematic showing the relationship of the semiconductor laser or light emitting diode (LED) array,

addressable radiation source to the printhead.

Figure 8 is a schematic of a semiconductor laser array integrated on a printhead.

Figure 9 is a schematic of a high throughput production system based on reel-to-reel flexible substrate transfer.

Figure 10 is a schematic of a light emitting polymer radiation source depicting ink curing adjacent to the printhead.

Figure 11 is a schematic of a linear addressable array imaging device (organic photoconductor array, etc.) integrated directly on to the printhead.

Figure 12 is a schematic of a whole area imaging system based on organic photoconductive array.

Figure 13 is a schematic of a radiation shutter and nozzle plate cleaning device integrated directly on to the printhead. Shows the triple acting wiper-blade scheme for real-time cleaning of the nozzle plate.

Figure 14 is a schematic of an ion implanted surface of the triple acting wiper-blade for improved tip stiffness and wear lifetime.

Figure 15 is a schematic of a bimorph transducer designed to provide real-time printhead height adjustment.

Figure 16 is a schematic of a localised environment control bellows structure associated with the region local to the printhead only.

Figure 17 is a schematic of a whole area microwave induced gaseous discharge that emits radiation from a single plane at a wavelength specific to the photoinitiator employed in the ink being printed.

Figures 18 to 20 are schematic diagrams relating to the manufacture of a radiation line source that is integrated on to the printhead and provides the transfer of radiation to the site of droplet impact and the region relating to a distance equivalent to a time after impact of 100 milliseconds.

Figure 21 is a schematic of printed wiring board via hole tenting method.

Figure 22 is a schematic of a common radiation curing system integrated on to a dual printhead arrangement.

Figure 23 is a schematic of chemical attachment printing using an ink jet printhead.

Figure 24 is a schematic of a dual printhead arrangement that permits back-to-front printing in parallel with a high pattern-to-pattern alignment.

Figure 25 is a schematic of an drop-on-demand printed ion implantation patterning mask.

Figure 26 is a schematic of a microvia-hole and containment well pattern mask.

Figure 27 is a schematic of an drop-on-demand printed stand-off spacer.

**[0071]** A preferred embodiment of the present invention employs, but is not limited to, the use of a XaarJet™ XJ500 printhead. This printhead has a print resolution of 180 dpi and a firing frequency of 4 kHz. Each nozzle has a diameter of 50µm that ejects a drop of diameter approximately 51 µm and volume 70 pL with a firing cycle delay of 83 µs. The nozzle geometry associated with the 500 nozzle nozzle-plate has a row stagger of 23.5 µm (customised nozzle plate unit).

**[0072]** This printhead is mounted in the printing system in such a manner as to permit y-axis movement (software-driven motor control) in order to print swathes of text/image data. The printhead can also be moved in the z-axis (software-driven motor control) in order to permit height adjustment in the range 0.1 to 10 mm. The substrate to be printed on moves in the +ve or -ve x-axis at a speed in the range 70 to 504 mm s<sup>-1</sup>, preferably at 280 mm s<sup>-1</sup>. The drive shaft encoder associated with the substrate movement has a resolution of 5 µm, with an associated print engine encoder divide factor of 14. Alternatively, a linear encoder with a resolution of 1 micron or below may be used for improved addressability. The resulting drop spacing in the axes perpendicular to the printhead is in the range 40 to 90 µm to match the image resolution, preferably 70µm.

**[0073]** The current process employs 2 passes per swathe, including a 70 µm step (or due to the use of 2 printheads or employing the Xaar XJ1000 printhead, or similar unit), to double the nozzle resolution.

**[0074]** As the image resolution may be imperial (dpi) then suitable addressability on the substrate will also be imperial, and the use of an equivalent encoder signal is required.

**[0075]** Ink used with the Xaar printhead is UV curing, cyan in colour (although any colour or clear ink can be specified), has a density close to 1, a viscosity in the range 9 to 30 mPa.s, and a surface tension in the range 22 to 32 mN m<sup>-1</sup>. This ink requires an irradiation energy density of 1 to 2 J cm<sup>-2</sup> in order to achieve a full cure state. The drop is ejected from a nozzle using a pressure pulse as a result of the electric field initiated shear in the piezoelectric ceramic. The drop has a impact velocity of approximately 6 m s<sup>-1</sup>.

**[0076]** A drop of UV curing ink impacts the surface and undergoes inertial damping and surface spreading before being solidified by the action of UV wavelength light being exposed to the ink causing chemical cross-linking. The UV curing is in two parts, the first being local to the printhead, and the second being a whole area hard cure process. The local cure (see Figure 1) is employed to achieve a controlled degree of chemical cross-linking or curing sufficient to control the spreading distance in order to limit the size of the feature being printed. The degree of UV exposure and the time and duration when such exposure occurs is controlled in order to permit the required drop coalescence needed to produce a continuous line of any geometry. In one embodiment a UVP spotcure source (SCL1-6) is employed which uses a 400 W Hg lamp (UV band A). The UV source has 6 outputs that are optically imaged onto the ends of 6 liquid



filled fibre optics. Each fibre optic lightguide is butted into an F.S.I. spot-to-line converter. The converter is based on a randomised fibre-optic bundle that is stretched to a specific geometry and end polished. The randomisation permits a greater overall homogeneity of light output (uniform irradiance) because the fibre local is a direct conformal mapping. The line converter has an irradiance output area of 75 mm x 4.6 mm, which allows a consistent cure across the full printhead width.

[0077] The time delay between the drop impact and first exposure to the localised UV irradiation is up to 1000 ms. The line converter fibre-optic system can be varied in height (z-axis, relative to the substrate surface) in order to reduce the on-set of UV irradiation to a delay time of order 15 to 20ms (see Figure 2). These factors are adjusted in order to allow optimum coalescence of the individual drops in all directions (perpendicular axes, curves, 45° bends, etc.) to obtain the best overall line edge straightness, cross-sectional profile, and solid quality.

[0078] The final whole area cure is achieved using a Fusion UV F300S curing system. This system uses 300 W per linear inch (1800 W total output) D-Bulb spectral emission (see Figure 3) to provide full curing of the ink at the optimum printspeed.

[0079] Copper clad printed wiring boards employed in a preferred embodiment are pretreated using a Scotchbrite pad lubricated with IPA, followed by an IPA clean. This pre-treatment facilitates the copper oxide inhibiting, chromate coating removal, as well as, introducing some degree of surface roughening to enhance the adhesion of the ink jet printed, etch mask pattern. Other pre-treatments are also undertaken including an electroless clean (typically, nitric acid chromate removal followed by persulphate microetch) or an anti-tarnish treatment, both of which provide a clean surface on to which an adhesion promoting film or agent can be deposited. Such processes are compatible with a range of standard industry methods. The resulting ink jet printed etch mask pattern has been shown to be adherent to a wide range of copper finishes and other surfaces, including stainless steel, aluminium, plastic, nickel electrode on a ceramic, ceramic, tetrahedrally coordinated carbon, diamond-like carbon, and glass. The solidified ink has been shown to be chemically resistant to, and physically adherent to the substrate in the presence of, a wide range of copper etchants, including those based on cupric chloride, ammoniacal, and alkali recipes.

[0080] After etching the mask pattern needs to be removed. This can be achieved in a number of ways, including wet (caustic solution, solvents [including dichloromethane, NMP, etc.]) and dry (reactive ion and inert plasmas) processes.

[0081] Next generation mask printing has already identified that the droplet size will become smaller, as per XaarJet™ XJ100 (360 dpi) or greyscale, where a drop size of 21pL of diameter 36.2µm will be available. The associated drop spacing will be in the range 25 to 40µm, and the nozzle row stagger and printhead firing cycle delay will be optimised to suit the printhead firing frequency. The resulting etch mask pattern will appear smooth as a result of edge (curve steps, etc.) in-fill with the smaller droplets associated with greyscale operation. Using this set-up the target line width is 50 to 100µm. Further system upgrades will cater for higher resolution printing, requiring more precise dot placement (i.e., linear encoded x-y movement to ≤ 1µm accuracy and repeatability).

[0082] Referring to Figure 1 the image shows, in plan view, the spreading behaviour of a single drop of ink. The key features are the symmetry of the spreading on a surface that is everywhere isotropic (set as a factor of the model) and the rate of spreading (at room temperature).

[0083] The ink employed in this simulation was a 100% solid polymer that had a viscosity of 10 to 30 mPa.s and a surface tension of 24 to 30 mPa m<sup>-1</sup>. The substrate surface was defined as having a wetting contact angle to the ink of 22°.

[0084] It should be clear from such an image that the placement position of subsequent drops with respect to the rate of spreading will affect the drop coalescence necessary to achieve a continuous patterning feature. Moreover, if the ink drops are not controlled with respect to the rate and extent of the surface coverage then a non-parallel edged line will result.

[0085] The inventor has realised the importance of the definition of the timeframe over which such control must be exercised and the methods used to achieve it. Computational fluid dynamic (CFD) modelling has been undertaken to study the fluid behaviour, which has been supported by high-speed imaging of droplet behaviour. The key processing requirement is to provide drop coalescence and curing in such a manner as to provide a straight-edge, parallel-sided line.

[0086] A particular feature of importance is the ability to control the lateral movement of the printhead in order to select a side-by-side droplet placement distance commensurate with the dot resolution required (subject to the size of the liquid droplet ejected and that actually impacting the substrate surface). The details of the feature to be printed dictate the edge definition that can be achieved with a specific printhead with associated drop diameter. The use of microdot grey scale levels, providing that individual drops can be software accessed/controlled, enables finer feature geometry to be achieved. The importance of this feature resides in the behaviour of the electrical circuit being defined by the mask pattern. The connecting conductor elements in a circuit are expected to be parallel, smooth edged, straight or curved features, ideally possessing no edge roughness. Edge roughening can contribute to signal degradation due to unnecessary scattering events. The detailed understanding of drop placement accuracy as a function of printing

mode and print speed, liquid droplet impact and interaction with the substrate surface, and manipulation of the masking material drying/curing is of paramount importance.

[0087] A particular importance with respect to this invention is the definition of an operating parameter space for the liquid droplet, irrespective of the print engine or printer operational mode employed.

- Ink viscosity (5 to 50 mPa.s) for a 100 % solid material
- Surface tension  $\leq 40 \text{ mN m}^{-1}$
- Droplet impact velocity  $\leq 10 \text{ ms}^{-1}$
- Droplet diameter  $\leq 50 \text{ }\mu\text{m}$

[0088] Figures 2[a-b] and 3 show the inertial dynamics and subsequent spreading behaviour of two droplets that are delayed in their time of impact by 250 microseconds (equivalent to a drop centre-to-centre spacing of  $70 \text{ }\mu\text{m}$ ). In order to achieve the smallest feature size for a specific ink (viscosity, surface tension, impact velocity, drop volume, etc.) on a given surface (surface roughness, surface energy, chemical stability to ink, etc.) printed in a specified environment (humidity, temperature, particulate density, etc.) it can be seen that the rheology of the ink must be stiffened to the point that movement (surface spreading) is arrested within a timeframe of 970 microseconds. If the spreading is allowed to continue before solidification is induced then the printed line will increase in linewidth until the spreading action is arrested by a balance between the surface capillary force and the ink surface tension.

[0089] It should be noted that changes to the ink, printhead, substrate material, printing environment will affect the time period that results in the correct coalescence of the sequence of drops required to print the image of interest. It should also be noted that wet drop coalescing with a solid ink dot (wet on dry non-wetting behaviour to be considered here) will promote a different time period for straight-edged parallel-sided features than that described for the wet drop coalescing with a wet drop outlined above. Changes in such properties do not fall outside of the scope of the invention. In order to achieve such control it is not possible to use a solidification process that is not integrated with the printhead.

[0090] The present invention provides the ability to select the time and location relative to the droplet impact zone when the light radiation is allowed to interact with the printed feature liquid ink.

[0091] A drop-on-demand ink jet printhead fires a single droplet (or series of droplets) of a specific ink formulation that is solidified at a precise time at the point of, or after, impact with the surface Momentum and surface capillarity induced drop spreading

0 to  $15 \mu\text{sec}$  - Surface contact with contact angle changing from  $> 130^\circ$  to  $< 90^\circ$ .

[0092] This is the region that would be used to control the cross-section profile of individual dots.

15 to $250 \mu\text{sec}$ -	Impact induced inertia completely damped
250 to $1,000 \mu\text{sec}$ -	Droplet coalescence promotes parallel-sided feature leading to the printing of a straight line.
$1,000 \mu\text{sec}$ onwards -	Ink rheology coupled with the difference in the surface energy and ink surface tension provides energy to promote continual spreading until ink irradiated to cross-link the UV curing polymer.

[0093] In a preferred embodiment of the invention, the ink formulation undergoes high speed curing when exposed to electromagnetic radiation. Preferably the electromagnetic radiation includes the wavelength bands assigned to Ultra Violet (including deep UV and UVA, UVB, UVC), Visible, and Infrared radiation (including far infrared), Microwaves, and  $\alpha$ -particles (alphas).

[0094] Figure 4 shows a schematic of the geometrical set-up of one embodiment of an ink jet printing masking system. In particular the schematic shows the substrate travel in the x-axis (direction of print - either positive or negative i.e., bi-directional printing with integrated light source on either side of printhead) at a rate dependent upon the ejection frequency and droplet size of the printhead employed. Printing in the y-axis can be by step-and-repeat swathes or by linear butting of multiple printheads to provide complete coverage with nozzles over the y-axis dimension (board length, etc.) of interest.

[0095] Figure 5 shows a schematic of the geometrical relationship between the printhead and the integrated light source, showing particular emphasis on the location and width of the irradiated area. Also shown is the z-axis height adjustment that affords control over the irradiation intensity. By way of example it is possible to consider a typical printing exercise based on the use of a Xaar XJ500™ printhead firing a UV curing polymeric ink. A typical process (see above background information) employs a substrate x-axis transport rate of  $280 \text{ mm s}^{-1}$  and a drop of volume  $70 \text{ pL}$  ( $70 \times 10^{-12} \text{ Litres}$ ) and  $51 \mu\text{m}$  diameter ejected at a rate of  $4 \text{ kHz}$  and a localised ink dot stitching irradiation energy in the range  $1 \text{ to } 200 \text{ mJ cm}^{-2}$  ( $2 \text{ to } 20 \text{ mJ cm}^{-2}$  most preferred) This provides a drop impact centre-to-centre spacing of  $70 \mu\text{m}$  (see Figure 6) for a printhead height above the substrate of  $0.1 \text{ to } 2 \text{ mm}$  ( $0.5 \text{ mm}$  most preferred). The resulting dot pattern is permitted to spread on the surface for a period of between  $80 \text{ to } 100 \text{ milliseconds}$  before being exposed

to the integrated UV line source ( area 70 mm in y-axis by 4.5 mm in x-axis). The resulting masking material line has a width of 140 $\mu$ m. Compensation due to errors relating to drop ejection jet angle, drop velocity, substrate speed, ejection timing have been ignored in the above example.

[0096] The method of irradiating the drop-on-demand impacting droplets does not have to be solely due to lamps or fibre-optic light-pipe-based systems. Figure 7 and 8 show schematics of preferred embodiments, the electromagnetic radiation means is an independently addressable array of semiconductor solid-state lasers or light emitting diodes (LED's - organic or inorganic). In such embodiments a solid-state semiconductor laser is used to irradiate a drop of fluid in-flight and as it impacts and resides/spreads on a substrate surface, thereby influencing the fluid properties both in-flight and on the surface to limit surface wetting (and hence solid dot/line cross-section, especially for 100% solid polymers) and interfacial impact effects. In order to test if this concept is technically viable then one needs to consider a few basic features. The expected drop velocity will be in the range 1 to 3 m s<sup>-1</sup>. For the purpose of example the figure of 3 m s<sup>-1</sup> will be used. Let us assume that the printhead-to-substrate distance is 2 mm. Also that the drop diameter is 50 $\mu$ m [microns] and the print speed (substrate movement relative to the printhead) is 0.5 m s<sup>-1</sup> with a drop eject rate of 1 kHz. Calculated transit time, allowing for the angular deviation of the drop flight path, is 1.37 milliseconds.

[0097] There will be a mechanical blind spot just in front of the nozzle-shutter assembly where the laser light beam cannot access the ejected drop. Due to a blind spot depth of 0.6 mm the available irradiation time, resulting from the remainder of the drop flight, will be 1.16 milliseconds. Assuming a 100 mW cm<sup>-2</sup> laser beam intensity and a simple linear absorption then the level of exposure would be 116 $\mu$ J cm<sup>-2</sup>.

[0098] The irradiation of the drop will not be uniform throughout the flight time. This is partly due to the absorption performance (light exposure photoinitiator loss profile) of the fluid drop and partly due to the homogeneity (concentration and distribution of photoinitiator) of the cross-linking that takes place at the surface and in the bulk of the fluid drop. In this respect one needs to understand the irradiation intensity (mW cm<sup>-2</sup>) and the exposure dose (mJ cm<sup>-2</sup>).

[0099] The rate of photochemical reaction depends firstly on the probability of an incident photon being absorbed by the selected photoinitiator molecule, and secondly on the concentration of photoinitiator employed. The objective of the initial in-flight and surface exposure is to promote sufficient cross-linking so as to limit or arrest the spreading action of the drop on impact. This necessitates absorbing the drop kinetic energy whilst still effecting an adequate adhesion of the cured drop on the substrate surface. If the laser beam profile is constructed to be a "top-hat" design and that the light intensity is above the required critical threshold, then it might be possible to consider a static irradiation process that covers the total accessible flight path of the drop. A second laser source, exhibiting a "top-hat" beam profile, continuously irradiates the substrate surface just in front of where the drop lands. The laser sources providing a parallel beam irradiation with constructive interference occurring at the point of drop impact. The actual interference area being an ellipse of minimum axis (65 $\mu$ m [microns]) 25 % greater than the drop diameter. The exposure time for the second laser is dictated by the substrate transfer speed and the "top-hat" geometry employed (for a 1 mm beam line width). The total exposure time is 2 milliseconds. If the "top-hat" beam had an intensity of 100 mW cm<sup>-2</sup>, then the level of exposure will only be 200 $\mu$ J cm<sup>-2</sup> [microjoules]. The clear issue is what intensity and level of exposure is required to photocure a 50 $\mu$ m [micron] diameter drop to a level sufficient to inhibit surface spreading (assume 20 % cross-linking in the absence of more accurate data). Also need to determine the change in viscosity with exposure level and the ensuing influence on the impact properties of a viscous drop on a solid surface. UV cured polymeric ink systems are currently employed in desk-top publishing and wide format printing of colour text and graphics. The standard process is to print the polymer onto a porous paper or treated paper or conventional/treated flexible plastic and allow the ink droplet to reach spreading equilibrium before irradiating with a suitable wavelength of light. This application discloses processing and system details applicable to the radiation processing of ink jet printable inks or fluids, especially UV curing inks with a view to enhancing print resolution.

[0100] The inventor has defined a design for a high throughput etch mask printing system based on both reel-to-reel and robotic substrate transfer methods. This is achieved by making use of multiple sets of printheads so arranged as to permit a multiplicity of work stations (see Figure 9) to be operational along the open length of the plastic sheeting retained between the two tensioned "feed" and "accept" drums.

[0101] A radiation curing source based on light emitting polymers (LEP's) that are employed in a strip light or whole area illumination device may also be utilised (see Figure 10). The radiation curing is achieved as a large area process by making use of thin film inorganic or organic light emitting materials. The thin film device design defines the wavelength band that will be emitted by the device. The emission can be tuned to suit a specific wavelength or wavelengths. Discrete stripes or bands of wavelength can be achieved in the device manufacture. Stripe or band focusing or defocusing can be achieved with a lenticular lens arrangement. The lenticular lens would also be deposited using drop-on-demand techniques.

[0102] Figure 11 shows a schematic outlining a means of dynamic print imaging using a linear imaging device integrated directly on to the ink jet printhead. Future systems will employ in-situ droplet impact imaging employing a fixed width charge-coupled device (CCD) [or x-y addressable] imaging array using co-incident nozzle-to-pixel geometry for real-time monitoring of printhead behaviour in relation to placement accuracy and processing yield (substrate rework).

Identification of faulty nozzles (dot/no dot identification) would permit a redefinition of the printing image in order to compensate for the observed faulty nozzles (Artificial Intelligence system operation). The imaging array being placed adjacent to the printhead nozzles in order to obtain localised individual nozzle-drop-dot behaviour. Another preferred embodiment of this invention makes use of a simple organic photoconductive pixel array with integrated organic lenslet array in place of the CCD or x-y addressable Metal-Oxide-Semiconductor silicon photodiode imaging array's.

**[0103]** Figure 12 shows a schematic of a means of enhancing processing yield by incorporating etch mask pattern recognition and software-based printed pattern overlay comparison using a large area organic photoconductive (photodiode) array. Large area being compatible with a direct 1:1 image mapping so that a complete printed circuit board could be imaged without the need to scan a camera over the board surface. Software then compares the mask pattern CAD image with the image captured from the large area organic photoconductor array. Defects observed would be identified by vector coordinates and if the defect is a missing section of mask then the ink jet printhead can be transferred to the correct location to repair the track.

**[0104]** Figure 13 is a schematic depicting a bimorph driven electromagnetic radiation shutter. The shutter assembly makes use of a silicon micromachined structure (MMS) that provides the necessary nozzle apertures, which are oversized compared to the actual drop diameter. The internal surface of the shutter assembly (silicon MMS) has fabricated on it a set of nozzle plate cleaning wiper blade-type structures, that are non-wetting to the ink and include easy-flow fluid ducting to permit the excess ink removed from the nozzle plate to be transferred to a catch reservoir at the edge of the printhead, which is periodically emptied using a simple vacuum suction nozzle. In operation the shutter assembly would normal act to cap the nozzle array, making use of the triple blade sealing on either side of the nozzle. The wiper blade type sealing stripes are sealed at both ends to form an enclosed capping arrangement. The firing sequence would be:

1. Standby mode the shutter assembly is positioned so as to cover the nozzle array.
2. Clean nozzle plate by oscillating the bimorph shutter backwards and forwards.
3. Test fire the printhead with a 50 pulse (50 drops) burst for all nozzles in the array. Excess fluid is drained towards the catch reservoir for subsequent vacuum suction removal.
4. Remove excess fluid from catch reservoir.
5. Download CAD image to be printed.
6. Use the leading edge of the drive waveform to trigger the bimorph shutter waveform in order to move the shutter into the firing position.
7. As the shutter reaches the firing position so the droplet begins to be formed at the nozzle exit.
8. Once the droplet is released and is clear of the shutter assembly the shutter is momentarily closed, thereby cleaning the nozzle between each jetted drop.

**[0105]** Future printheads will employ drive waveforms that accurately control the timing sequence of order for drop eject, bimorph nozzle shutter micropositioning, and solid state semiconductor laser pulse activation for a "smart" fluid jetting module operation. The nozzle drive pulse can also be monitored, on suitably manufactured printheads, leading to:

- modification of firing delay to impact placement accuracy.
- gradual change in firing parameter(s) to maintain a given droplet set of properties.
- generation of printing test pattern and image grabbing and interpretation leading to software manipulation of placement accuracy versus specific nozzle drive properties.

**[0106]** The in-situ environmental and radiation shutter assembly also acts as a:

- real-time pulsed plasma electrode that provides surface pre-treatment adjacent to droplet landing zone.
- printhead vacuum priming unit.

The wiper blade nozzle plate cleaning material wants to be compliant, tough, adherent to the substrate, and chemically stable in contact with the fluid/ink system being jetted. Typical materials include, silicone, polyimide, PTFE, rubber, neoprene, polyvinyl, and viton. The surface of the wiper blade feature can be locally hardened (see Figure 14) to provide a better cleaning action and wear resistance by exposing the surface to a beam of high energy ions (ion implantation or plasma immersion implantation). A typical process would be to use  $10^{15}$  ions  $\text{cm}^{-2}$  of nitrogen implanted into say Teflon coating at an energy of 70 keV, to produce a total range of ion uptake of 231 nm.

A number of droplet firing waveforms and sequences catering for variable speed radiation curing printing, which includes very high speed, may be required to support the wide variety of applications making use of this technology. Very high speed includes the situation where the piezoelectric or relaxor type ink jet printhead is operated in a resonance mode (up to approximately 1 MHz or so).

Surface pre-treatments in-situ, and prior, to printing an etch mask or surface relief pattern, may be required to ensure adequate adhesion and to limit surface wetting. The means of providing the surface cleaning being based on localised creation of ozone, UV exposure, acidic or alkali jetting from a spray head or an ink jet printhead, or solvent dispensing from a spray head or an inkjet printhead, including a means of drying. A number of manufacturers make printed wiring board substrate material. In most cases the metal is copper and is either vacuum or adhesive laminated on to the substrate of choice (FR4, PTFE, polyimide, etc.). Invariably this means that the surface quality from each is different either in texture on a microscopic scale or in planarity (reinforcing fibres, foil rolling stress lines, etc.) on a macroscopic scale.

- Ozone plasma
- Specific plasma
- Localised UV irradiation

All of the above substrate pre-treatments are to be considered for compatibility with both wet and dry etching methods. This is because the etch mask printing process can be applied to surface other than copper, that are not necessarily compatible with high resolution wet etch processes. It is a preferred embodiment to consider printing a negative image of the image to be achieved with the masking layer. This negative image being a non-wetting coating that affords limited spreading of the masking material. In order for this technique to work it is important that the printing parameters and masking ink are selected so as to inhibit splashing and excessive inertial effects upon drop impact. If this occurs then "over-wash" can occur that if the receding angle is high will result in ink spreading over the negative non-wetting control print.

**[0107]** Preferred embodiments of the present invention can provide real-time height positioning of an ink jet printhead using a bimorph positioning transducer that permits printhead movement in the z-axis (see Figure 15). Height adjustment is preferably in the range 50 to 200 microns. The tip deflection distance of a bimorph cantilever is proportional to its length, as given by  $x(L, V) := 2.3/2 \cdot d_{31} \cdot L^2/t^2 \cdot V$  ( $t$  = bimorph thickness;  $L$  = bimorph length;  $d_{31}$  = charge constant [i.e.,  $-306 \times 10^{-12}$  CN<sup>-1</sup> for Morgan Matroc PCK<sub>5</sub>];  $V$  = drive voltage). For a drive voltage of 100 volts and a bimorph length of 15 mm expected tip deflection will be approximately 100 microns at a free resonance frequency of 1,200 Hz. Bimorph height control of printhead using semiconductor laser height range finder with feedback to bimorph. Bimorphs positioned at either end of printhead. Real-time adjustment of height to facilitate very close proximity printing of less than or equal to 250µm (microns). Real-time position is a direct result of feedback signal from electro-optical (laser [range finder principle] or LED in conjunction with a phototransistor or photocell pair) or capacitive sensing element. In the limit the height control would lead to direct transfer contact wherein the ink is not fired as a droplet at all but is transferred on to the substrate surface via differential wetting action that forces the pressure induced droplet "Necking" to break. Head height control can also be due to inductive sensor response for metal substrates.

**[0108]** It is anticipated that temperature and atmosphere control of the operating zone adjacent to the printhead will be required. Such localised atmosphere control (see Figure 16) provides a much cheaper means of controlling the required deposit than that due to atmosphere control associated with the whole area to be printed on. The control zone is defined as the area bounded by the printhead nozzle plate in the +ve z-axis and the substrate surface in the -ve z-axis, and the length and width of the nozzle plate including a factor that allows for edge effects. This zone can in one embodiment be achieved by surrounding the printhead and integrated dot imaging and radiation curing source in a bellows-type structure that provides a positive pressure of air or a specified inert or reactive gas injection (gas being heated or cooled). A soft vacuum can also be supported within the bellows, making use of a dry vacuum pumping arrangement. The bellows structure will be made of a soft, flexible, low gas permeability, electrically conductive material that both assists surface cleaning and surface electrical charge dissipation. The etch mask material printing and cure will take place inside this envelope. Close proximity printhead head to substrate spacing requires consideration of:

- electrical potential across the printhead-to-substrate gap as contained within the processing bellows.
- vacuum suction and air flow induced pressure differential in the processing bellows.
- air flow filtering to minimise particulate accumulation in the printhead-to-substrate gap by filtration of the air or gases used in the processing bellows. If vacuum employed then particulate in-take would be minimised by presence of bellows. Consideration to be given to the height between base of bellows and the substrate surface.

**[0109]** For high throughput printing it is preferable to employ a wide format printing capability by fabricating a printhead enclosure that can house a multiple of printheads. This is achieved by butting together a series of printheads with a common nozzle format. This is required to ensure that although the number of nozzles is increased the resultant parallel-sided pattern is not affected. The butting error could compromise such print, hence the need to integrate a common nozzle plate. The close coupled (butted) printheads are aligned in x-y-z axes by utilising piezoelectric positioning of a He-Ne sighting laser assembly that can be removed once the alignment has been completed and the set-up locked in position. Such positional accuracy is essential if the geometrical limitations of the etch mask pattern is to

be maintain across the substrate surface to be coated. Another preferred embodiment is to use a multiple printhead alignment using piezoelectric positioners that employ a feedback-loop driven by the in-situ imaging of ejected drops on to a set of test patterns that are imaged and overlaid on to the test pattern to define the nature and degree of feedback control required.

**[0110]** Ink formulation for optimisation of the mask pattern linewidth control have been studied. It has been shown that the glass transition temperature,  $T_g$ , affects the hardness and temperature stability of the current acrylate ink, without adversely affecting the viscosity and surface tension of the ink. It has been shown experimentally that changes in the bulk-to-surface photoinitiator ratio also affect the rate of curing. Changes to the photoinitiator ratio in the range 1:1 to 4:1 (surface:bulk) have been shown to promote faster curing. Too high a surface initiator content promotes in-nozzle blocking before droplets can actually be ejected. A range of fluid properties must be optimised in order to provide a minimum in the droplet surface spreading and hence the linewidth and cross-sectional profile of the mask pattern, irrespective of whether the ink drop is solidified by air drying, or by radiation, curing methods. Such properties include:

Droplet velocity	= 0.1 to 10 [ $\text{m s}^{-1}$ ]
Dynamic viscosity	= 1 to 100 [ $\text{mPa.s}$ ]
Heat of vapourisation	= Low [ $\text{J mol}^{-1}$ ] (Liquid dependent)
Liquid density	= 0.5 to 1.8 [ $\text{kg m}^{-3}$ ] (Liquid dependent)
Material solid content	= 0.0001 to 100 [%]
Static contact angle to the substrate	= 0 to 120 [ $^\circ$ ]
Substrate temperature	= 230 to 370 [K]
Surface tension	= 35 to 76 [ $\text{mN m}^{-1}$ ]

**[0111]** The ratio of bulk to surface photoinitiator also has an effect on the rate of solidification. This is also the case for the surface tension and the glass transition temperature,  $T_g$ , of the polymer used for the mask. In a preferred embodiment the ink formulation is compatible with the operation of an integral fluid nanoscale filter, which is based on Lamb wave fluid transport principles, where the fluid is flowed through a porous silicon etched (chaotic) filter structure. Lamb wave electrode design for fluid transport through filter and for providing controlled fluid feed to the nozzle. Provides for precision metering of fluid and timing of arrival at the nozzle bore.

**[0112]** The present invention can also provide a means of large area polymer cross-linking (for extended time or hard cured etch mask material solidification) by making use of a close proximity (to the printhead assembly [x- and y-axes] and to the substrate surface [z-axis]), low temperature (not requiring any assisted cooling), microwave initiated gaseous discharge radiation source (see Figure 17). The gas discharge radiation source provides illumination on to the substrate surface only because the upper surface of the assembly has had deposited on it a thin film coating that reflects light back into the body of the discharge (light guide), thereby enhancing the coupling-out efficiency, and the lower surface has had fabricated in it a surface relief pattern that permits the discharge induced photo species to couple-out on to the substrate surface and thereby irradiate the mask material. The surface relief required to extract the plasma discharge photons of the desired wavelength (gas specific) can be a dispersion structure such as diffuser, dot matrix, or moth-eyed lens matrix.

**[0113]** A preferred embodiment makes use of lenticular lens type array, where the nearly rectangular cross-sectioned (variable angled wall geometry of angle  $\leq 90^\circ$ ) projection width, height, and wall slope affect the efficiency of coupling for the wavelength of light specified. The light guide and gas discharge (plasma) confinement structure are made of quartz or similar UV transmitting material. The close proximity assembly assists the transfer of photo energy ( $\mu\text{J}$  or  $\text{mJ cm}^{-2}$ ) without significant loss due to the path length (inverse square law effect). In a preferred embodiment whole area microwave initiated gas discharge supported UV irradiation will be used for large area panel final cure exposure. The grating structure outlined above is designed to match the wavelength of light, which is dictated by the gas chemistry employed. Such gases include Ar, He, Cl, Xe,  $\text{O}_2$ ,  $\text{N}_2$ , etc. and mixtures thereof

**[0114]** Another preferred embodiment of the grating structure is a set of rectangular features that replicate a "castle turret" type geometry forming peaks and troughs. The mark-space ratio and the geometry of the mark rectangle (height and width and wall slope) depend upon the wavelength of light to be coupled out of the window surface.

**[0115]** In a preferred embodiment the reflecting surface (thin film aluminium, gold, etc.) can be included on the outside of the upper (roof) of the enclosure to enhance the efficiency of the output of the exposure unit. This UV curing unit would operate at power levels that would not require noisy and bulky air cooling. Recirculating gas cooling can be introduced if high power applications are required

**[0116]** A specified nozzle plate geometry may be provided to affect the placement control of the drops ejected from the nozzle array. Not all printheads eject ink drops from adjacent nozzles simultaneously. This is because for piezoelectric-based ink jet printheads the mode of operation can be due to a bending, pushing, or shearing action. If shearing action is employed (i.e., Xaar XJ series printhead) then a nozzle stagger must be defined in the nozzle plate to permit

straight text printing. In order to obtain a coalescence of drops, leading to a well defined line, it is necessary to vary the drop spacing by operating the printhead outside of standard parameter range. For the Xaar printhead the firing delay implies a substrate movement that leads to a series of drops being printed on a stagger. In order to achieve a straight line process a number of potential solutions are possible, namely:

1. Reprogram the cycle time delay to another fixed value.
2. Fabricate a nozzle plate with a different nozzle stagger.
3. Change the image processing to increase resolution.
4. Reprogram the chip with a single cycle waveform i.e., all channels fire at the same time and use image processing to cater for the fact that this is not practical (implication on print speed).

**[0117]** A preferred embodiment of the invention provides for a specific set of nozzle plate designs to cater for the ink jet printing of a mask pattern that has a parallel line width in all direction on an x-y plane.

**[0118]** The present invention can be extended to a method of ink jet printing an electrode surface solder mask pattern. In this instance the method used to form the solder mask is similar to that used to form the etch mask defined above, with the difference being that the choice of ink formulation must reflect the higher temperature limits applied to the solder dip coating and thermal wave solder reflow processes. The solder mask is designed to provide a means of limiting the region of a suitably treated surface that can be coated with a solder metal such as In, Sn Pb-Sn alloy, etc. Soluble materials that can be used as the solder mask include silicone, polyimide, PTFE, and epoxy.

**[0119]** The present invention can provide a method of achieving a 3-D etch mask using ink jet printing methods. A number of device fabrication applications require the production of a variable build height or etch depth feature. It is possible to use the ink jet printing process to define such a feature using either multiple drops solidified at a specific site or multiple passes of a pattern where the pattern being printed can be different each time. In either case the mask being generated has a local change in height profile. The mask can either be left as a solid structure forming a 3-D relief structure on a surface or can be used in an etch process whereby the mask material is progressively etched over time by the etchant. The progressive etching promotes a local change in etch depth, particularly for a reactive ion beam or plasma dry etch process. The mask material can be of a single type with the progressive etch rate being constant and the etch depth change being due to the variation in thickness and hence the rate of mask consumption to expose the surface undergoing controlled etching. The mask can also be made up of a number of materials that have different etch rates (etch resistance) to the etchant employed. In this case it is possible to define a completely robust etch mask at a specific location in the mask build, thereby permitting etch control in x, y, and z (depth) axes.

**[0120]** A UV (or alternate energy/radiation) line source may be used in the manufacture of an etch mask pattern. Such a line source may be required to provide a uniform area of radiation (UV-visible-IR-electron) exposure across the width of the selected printhead and to provide a specified area of exposure and for the exposure to occur at a specific location relative to the drop impact zone. The line source can make use of a fibre-optic bundle that is fanned-out to give a single line of fibres of individual diameter in the range 0.25 to 1 mm (see Figures 18-21). The line of fibres are in direct contact and are secured to a polyimide sheet backing material that provides some degree of rigidity and ease of handling. The flexibility of the fibres and the backing sheet permit the fibre bundle to be shaped to the correct position and angle for radiation exposure at, or adjacent to, the drop impact zone. The front surface of the fibre bundle can have bonded onto it a lenticular lenses that provides a high degree of light homogenisation across the whole array of individual fibres. A number of such fibre bundles can be constructed that provide a set of irradiation zones that are deliberately overlapped to form a large area exposure or are left isolated to provide pulsed exposure at, and for, set time intervals as the substrate traverses the irradiation zone.

**[0121]** Alternatively, local curing may be achieved using a xenon lamp with variable duty cycle, operating frequency and spectrum (by using filters and/or doping of lamp gases and/or varying power supply to lamp).

**[0122]** The present invention can be extended to a method of covering (tenting) printed wiring/circuit board plated through-holes using the ink jet printing process (see Figure 21). Typical plated through-holes range in size from 0.1 to 1 mm in diameter. The tenting process can be approached in two ways, namely, plated hole in-fill or surface tension driven coating.

**[0123]** The in-fill process makes use of a multiplicity of droplets that under the action of capillary forces causes the droplets to fill the plated hole. UV curing solidifies the fluid to form a solid plug.

**[0124]** Surface tension driven coating process requires that the drop size be greater than the size of the hole to be covered. Moreover, the surface tension of the fluid needs to be control so as to limit the degree of surface wetting, whereupon the fluid surface tension restoring forces will tend to make the fluid take on a hemispherical geometry that covers the plated hole as desired. The fluid is again solidified by exposure to radiation (UV-visible-IR-electron).

**[0125]** The techniques described above can be extended to a method of removing an ink jet printed UV cured acrylate etch mask. The removal process can be either dry or wet. The dry process makes use of a plasma based on a variety of gas chemistries including argon, oxygen, argon-oxygen mix, CF<sub>4</sub>-oxygen mix, argon-water vapour, etc. (Inert gas

rare-earth series; Reactive gas being hydrogenated, oxygenated, chlorinated, fluorinated, etc.). The inert gas, such as argon, provides an ion that bombards the masking material with a view to disrupting the surface/near-surface regions (termed "Altered Layer"). This disrupted zone permits easy transport of reactive species in to the bulk of the masking material, as well as, providing direct access for such species to the exposed carbon backbone of the acrylate chemistry.

The electronegativity of the competing species (i.e., C-C, C-H, C-O, C-F, etc.) coupled with the extraneous energy dissipated by the hot (high energy) ion provides the necessary thermodynamics to permit high rate etching of the acrylate to occur due to place exchange reaction. Etch rates in excess of 1  $\mu\text{m}$  [micron] per minute are readily achievable.

**[0126]** The wet process can make use of both aqueous and non-aqueous solvent systems. Aqueous based chemical etchants are primarily caustic-based [typical process being spray injection via roller feed of 5% NaOH in  $\text{H}_2\text{O}$  at 30°C].

The non-aqueous solvent used to remove the acrylate mask include:

- Chloroform (dissolution action)
- Dichloromethane (swelling and dissolution action - quick removal)
- Tetrachloromethane (dissolution action)
- Chlorobenzene (swelling action)
- 1,1,2-trichloroethane (dissolution action)
- N-methyl pyrrolidinone [NMP] (swelling action - slow process)

**[0127]** Similarly, the above techniques can be applied to a method of ink jet printing of dry etch resistant, inorganic etch mask. Although the etch mask process described above makes use of an acrylate (organic) material the ink jet printing method can equally provide etch masks based on inorganic or mixed organic-inorganic fluid systems. In such cases the properties of the fluid and chemically stability with respect to the printhead materials and nozzle non-wetting coating still apply.

**[0128]** The method used to solidify the drops may be dictated by the fluid system employed. An organic-inorganic fluid (ormocer - organically modified ceramic, sol-gel, metallo-organic, etc.) can still employ radiation curing, such as UV. However, dependent upon the application a further level of solidification will be required that makes use of thermal densification. In this case either rapid thermal methods can be applied using close proximity irradiation or sequential transfer to a processing zone. The thermal annealing process is used to densify the mask material and to drive out high etch rate organics. The ensuing material then possess a specified degree of radiation (plasma) hardness that makes it suitable for dry etch masking applications.

**[0129]** The present invention also extends to a method of drop radiation curing making use of a dual printhead arrangement with a common integrated radiation curing source (see Figure 22). This arrangement has a radiation source located at the outer edges and the centre of the dual back-to-back printhead arrangement. This permits the printhead to print in a bi-directional mode, providing the same degree of radiation exposure irrespective of the forward or reverse direction print.

**[0130]** The above described techniques can be applied to a method of ink jet printing of electroless and electrolytic plating bath resistant, etch mask patterns. The method of printing is the same as for printed wiring board etch mask printing. The difference is in the choice of materials used and the need to construct a mask pattern that is 3-dimensional in nature. The 3-D printing has been described above. The selection of the mask material depends upon the specifics of the electroless and/or electrolytic plating bath solution chemistry. Typical materials include epoxies, polycarbonates, silicone, PTFE, polychlorotrifluoroethylene, polyimide, polyisoprene, and polypropylenepolystyrene, etc.

**[0131]** An additive plating etch mask may also be formed using ink jet printing. This is a specific use of localised height build, as covered under the 3-D printing heading above.

**[0132]** Additionally a high resolution etch mask may be formed using ink jet printing. High resolution has a different meaning dependent upon the application being served. For the purpose of this disclosure high resolution means a feature size of less than 10  $\mu\text{m}$  [microns].

**[0133]** An electrically conducting masking layer can also be formed using the above described techniques. Such a masking layer can be left in place after use, as in the seed layer for electroless/electrolytic plating of an electrode pattern. The masking layer can be carbon-based or metal acetate-based (i.e., palladium), in order to effect a specific conductivity and chemical interfacial reaction prior to plating up with the metal of choice.

**[0134]** A decorative surface etch mask may also be formed. The decorative surface may be based on the properties of the ink(s) being used to form the surface relief pattern. By way of example it is possible to use an optical particle-loaded ink that upon solidification reflects light at different wavelengths dependent upon the exposure wavelength and angle. Such a system could be used as a security device due to the unique nature of the particulate distribution in the solid that can be imaged and recorded as a secure signature.

**[0135]** A mask pattern may be formed based on chemical attachment transfer (see Figure 23). Chemical attachment can be through chirality or via a hydrophilic-type reaction on a catalysed surface. The attached energy provides a means of transferring a known volume of fluid from a close proximity partially fired droplet, ensuring that the droplet



ligament breaks under controlled conditions. Computational fluid dynamic modelling has shown that such fluid transfer (FlowScience) does occur under specified fluid surface tension and substrate surface energy conditions.

**[0136]** A single panel printed wiring board (PWB) back-to-front auto-registered etch mask may be formed (see Figure 24). The process can make use of two facing printheads or butted linear arrays of printheads, that have been aligned relative to one another using for example a He-Ne laser beam and a silicon diode photodetector. The alignment being effected using piezoelectric bimorph positioning devices (or similar) of the x-y-z axes and the orientational azimuth of the printhead/printhead array. Once alignment has been effected then a panel can be transported in a frame to positioned midway between the printheads (or arrays) and a dual print achieved on both surface that register to a very high degree.

**[0137]** Near vertical-walled mask patterns may be formed. Computational fluid dynamic modelling (based on FlowScience Inc., Flow3D modelling software) of ink jet printhead ejected drop interaction with solid surfaces has suggested that it is possible to create a single dot with a sidewall geometry very close to vertical. The drop spacing and the solidification state of the previous drop, coupled with the impact velocity of the drop and the ink viscosity, affect the rate of coalescence to form a line. In order for the line to have a vertical sidewall profile it is essential that the coalescence process occurs in the time it takes for the drop material to spread-out to the width of the solidified drop (i.e., in a time  $\leq$  to 10  $\mu$ seconds).

**[0138]** An ion implantation mask may be formed (see Figure 25). The objective of the masking material is to shield the surface under the mask from a high energy ion beam. The energy range of interest spans 10 eV to 50 MeV. The masking layer thickness will depend upon the energy of the irradiating beam. For the highest energy the anticipated mask thickness will be  $\leq$  10  $\mu$ m.

**[0139]** The present invention may extend to a method of producing a surface relief pattern on a surface. Such a relief pattern could be a confinement well mask used in the manufacture of a single or multiple colour light-emitting polymer displays (see Figure 26). Other such display devices that could make use of such a containment well include inorganic lanthanide dyes or organic small molecule dye structures.

**[0140]** The present invention may also extend to a method of producing a stand-off spacer pattern (see Figure 27). The stand-off spacer being used to separate, by a known and precise height, two parts of a flat panel display device. An example is the use of a spacer material, of a known conductivity and secondary electron emissivity, for use in a vacuum-based field emission display. A further example is the separation well structure used in a liquid crystal display. The well structure contains the liquid crystal that can be either ink jet printed or vacuum impregnated in order to effect filling of the well.

**[0141]** In alternative arrangements, an etch mask may be formed using an all-dry, charged toner, photo-transfer process. This is an adaptation of photocopying in that the toner is a nano- or microcapsule/particulate/bead system that provides the necessary dimension and material properties for charge accumulation on the toner and particle transfer to the photoconductor and substrate to be patterned. A computer generated image (CGI) is fed to a light emitting polymer (LEP) display that irradiates, at a specific wavelength or waveband, the photoconductive (photoreceptor) drum/plate containing the electrostatic charge. As in a standard photocopier the electrostatic charge (positive) retained on the photoconductive drum/plate fades where light from the LEP display is incident. A roller system transfers toner (negatively charged) to the image area on the photoconductive drum/plate. A substrate is brought into close proximity and the toner is transfer from the photoconductive drum/plate to the substrate. The substrate has been given a sufficient strong positive static charge to draw the image pattern in the toner away from the photoconductive drum/plate and to provide sufficient electrostatic attraction to hold the toner in place. At this point the standard photocopier process can be continued, namely toner fusing to substrate via heated roller pressure. Alternatively, the toner can be processed using in-situ rapid thermal/infrared radiation (pulsed or continuous irradiation) processing means to reflow the microcapsules/particles/beads in order to effect material coalescence. By way of example, consider that the toner microcapsules/particles are in fact solid beads of a low temperature ( $< 200^{\circ}\text{C}$ ) thermoplastic. The charged particles undergo melting as the temperature is introduced. The degree of melting being sufficient to permit coalescence without excessive surface wetting (reflow). Removal of heat permits the thermoplastic to resolidify, thus forming the required etch mask pattern. It is anticipated that hollow capsules could be used that contain a specific material (i.e., polymer, inorganic, etc.). Upon exposure to the correct radiation/processing atmosphere the shell of the microcapsule will disintegrate revealing the material inside. This material, having controlled viscosity and surface tension (temperature dependent), flows out of the corrupted containment shell and coalesces with material from nearest neighbour capsules, thus forming the necessary patterned image. Such an image need not be limited to an etch mask pattern but could form part of an organic electronic or opto-electronic device. The CGI pattern transfer means that no masks are required for this process.

**[0142]** Some examples embodying the present invention will now be described.

## General Features

### 1. Interlacing of images and printhead addressability

[0143] The circuit image is generated on a CAD/CAM system and exported to the mask print system in a standard vector format, such as RS-274X gerber. The file containing the circuit image is then converted to a raster format in order to produce the correct file type for printhead operation.

[0144] The raster image is also divided into swathes of an equal or lesser width to the printhead ready for printing. The image is further divided into a number of additional interlaced passes within each swathe in order to generate greater image resolution.

[0145] Channel stepping is an important issue in the field of etch mask printing as it allows increased addressability of drops onto the substrate than that produced using the printhead in its standard configuration.

[0146] The printhead is indexed by a value equal to

$$I/\text{number of passes} \times \text{the nozzle spacing}$$

For example in the case of a printhead with a nozzle resolution of 180 dpi, an image resolution of 360 dpi may be achieved by using 2 passes within each swathe with a  $\frac{1}{2}$  channel (70.5 micron) channel step incorporated. The image will be different for each pass within the swathe, in the case of 2 passes each pass image will contain alternate pixel lines.

[0147] For a 720 dpi drop addressability on the substrate 4 (that is, 720/180) passes are required, so that for a 720 dpi substrate addressability the printhead step index is  $\frac{1}{4} \times 141.1$  microns = 35.275 microns

[0148] In the case of a 4 pass process each successive image pass will contain every 4<sup>th</sup> pixel line.

[0149] It is envisaged that future printhead developments may give 16 level greyscale with smaller drops and 360dpi nozzle density. In this instance for 2880dpi drop addressability on the substrate, 8 (that is, 2880/260) passes are required. For this 2880dpi substrate addressability, the printhead step index is:  $\frac{1}{8} \times 70.6$  microns = 8.82 microns

[0150] An addition to this interlacing process is that subsequent passes within a swathe are carried out using a different set of nozzles. For example when using a 500 nozzle printhead then the image is divided into swathes / passes of between 400 and 496 pixel lines. The printhead may then moved by a whole number as well as the fractional step between channels, with the image adjusted in software to realign the image correctly. This approach minimises the impact of nozzle variations or failures, reducing pinhole formation and open circuit failure rates in the circuit produced.

[0151] For example the printhead may be indexed by  $5 \frac{1}{4} \times$  nozzle spacings between passes with the printhead channel offset parameter increased by 5 in order to realign the image.

### 2. General copper laminate pretreatment

[0152] All types of copper laminates, for example, standard HTE, reverse treated, double treated, chromate treated on both FR4 and PET substrates are subjected to the particular pretreatment regimes. A persulfate microetch is used to remove the anti-oxidant layer. Alternatively, pumicing, brushing or polishing the surface can also give satisfactory results. The surface roughness is typically in the range 0.1 - 5.0 microns, preferably 0.1 - 1.0 microns.

[0153] A proprietary anti-tarnish spray along with an adhesion promoter is then sprayed onto the board. The surface energy of the pretreated boards is within the range 24-35 dynes/cm, preferably 26-28 dynes/cm. Finally, a tacky roller or ioniser is used to remove any dust specks from the pretreated boards before printing.

### 3. General conditions

[0154] Etch mask printing has been carried out in a dust and vibration free environment, at ambient temperatures in the range of 10- 40°C, preferably 20-30°C at an ambient humidity which is preferably between 20 and 70%. The printhead temperature for all of the examples was in the range 30 - 60°C, preferably 35 - 45°C.

#### Example 1: Large feature sizes

[0155] The large feature size work (over 250 microns) was carried out using a Xaarjet XJ500 180 dpi printhead, designed to print UV curing acrylate based fluids, and constructed to a nozzle stagger of between 15 and 47 microns. The stagger used in this example was 23.5 microns. This printhead had 500 nozzles and produced dropsizes of volume 70 pL. The printhead was used at a height of 0.5 - 2.0mm above the substrate, preferably a height of 0.75-1.25 mm was used. The printhead addressability was in the range 180 -540 dpi, preferably 360 dpi, and printing performed in two directions at a printing speed of 168 -506 mm/s, preferably 282 mm/s. The drop impact /UV local cure delay was

## EP 1 163 552 B1

in the range 10 - 2000 ms, preferably 50-300 ms.

### Example 2: Medium feature sizes

[0156] The medium feature size work (over 150 microns) was carried out using a Xaarjet XJ500 360 dpi printhead, designed to print UV curing acrylate based fluids, and having a nozzle stagger of between 6 and 23.5 microns, preferably 11.8 microns. This head has 500 nozzles and produces dropsizes of volume 21 pico litres. The printhead was used at a height of 0.5 - 2.0mm above the substrate, preferably 0.75-1.25 mm. The printhead addressability was in the range 360 -1440 dpi, preferably 720 dpi and printing conducted in 4 passes in one direction at a printing speed of 60 - 506 mm/s, preferably 60 - 282 mm/s. The drop impact /UV local cure delay was in the range 10 - 2000 ms, preferably 50-300 ms.

### Example 3: Small feature sizes

[0157] The small feature size work (over 50microns) was carried out using a Xaarjet XJ500 Greyscale (8 levels) printhead, designed to print UV curing acrylate based fluids, with a nozzle stagger of between 3 and 11.8 microns, preferably 6.0 microns. This head has 500 nozzles and produces dropsizes of between 5 and 6 pico litres per level. The printhead was used at a height of 0.5 - 2.0mm above the substrate, preferably 0.25-1.25 mm. The printhead addressability was in the range 360 -1440 dpi, preferably 720 - 1440 dpi and printing conducted in 4 -8 passes, relative to the number of printheads used, in both directions at a printing speed of 43 - 350 mm/s, preferably 87.5 - 175 mm/s. The drop impact /UV local cure delay was in the range 10 - 2000 ms, preferably 50-300 ms.

[0158] It is envisaged that future printhead development providing 16 levels of greyscale with smaller dropsizes and increased nozzle density to 360dpi, will enable the addressability range range to extend to 2880dpi, with a print speed limited to the firing frequency of the printhead. Printing will be in the forward and reverse directions with 8 print passes (divided by the number of printheads used).

### 4. General UV ink curing conditions

[0159] The ink jet etch masking system is configured with two distinct UV curing sources: (i) a local curing source close to the printhead, with intensity in the range of 1 - 300 mW/cm<sup>2</sup>; and (ii) a final, full board curing source of intensity between 100 - 300 W / linear inch, with a total energy of between 0.5 and 4 J/cm<sup>2</sup>, and preferably 1-2 J/cm<sup>2</sup>.

[0160] Curing is preferentially conducted under a partially oxygen reduced atmosphere, normally, but not limited to, a positive pressure of nitrogen or other inert gas in the curing areas. The residence time under the final UV cure is between 1 and 10s.

[0161] Alternatively, local curing may be achieved using a xenon lamp with variable duty cycle, operating frequency and spectrum (using filters and/or doping of lamp gases and/or varying power supply to lamp).

### 5. Etch and mask pattern stripping conditions

[0162] The copper laminate board with the completed mask pattern is processed through a standard spray conveyor etch system using either acidic or alkaline etch chemistry.

[0163] The etch mask is then removed using an alkaline dip, preferably a caustic solution of potassium or sodium hydroxide/2-aminoethanol system at a temperature of between 20 and 50°C, and with agitation such as spray immersion.

## Claims

1. A method of forming a masking pattern on a surface, said method comprising the step of:

using the technique of drop-on-demand printing to deposit from droplet deposition apparatus a plurality of droplets on to a surface to form a masking pattern, said droplets passing through an operating zone located between the deposition apparatus and the surface, **characterized in that** said method further comprises the step of

locally exposing the operating zone to electromagnetic radiation so as to control coalescence of droplets on the surface, thereby controlling the solidity of the masking pattern.

2. A method according to Claim 1, wherein the formation of the masking pattern is controlled so that the masking

pattern has predetermined structural properties.

3. A method according to Claim 1 or 2, wherein the operating zone extends from the deposition apparatus to the surface.
4. A method according to any preceding claim, wherein relative movement is effected between the deposition apparatus and the surface so as to move said operating zone across the surface during formation of the masking pattern.
5. A method according to any preceding claim, wherein the local environment of the operating zone is controlled so as to control the coalescence of the droplets on the surface.
6. A method according to any preceding claim, wherein the local environment of the operating zone is controlled so as to control the spreading of the droplets on the surface.
7. A method according to any preceding claim, wherein the local environment of the operating zone is controlled so as to control placement of the droplets on the surface.
8. A method according to any preceding claim, wherein the local temperature of the operating zone is controlled so as to control the rate of solidification of the droplets on the surface.
9. A method according to any preceding claim, wherein the local atmosphere of the operating zone is controlled.
10. A method according to Claim 9, wherein an at least partial vacuum is generated in the operating zone so as to substantially avoid contamination of the droplets during passage from the deposition apparatus to the surface.
11. A method according to Claim 9 or 10, wherein a pressure differential extending between the deposition apparatus and the surface is established in the operating zone.
12. A method according to any of Claims 9 to 11, wherein an inert or reactive gas is introduced into the operating zone during droplet deposition.
13. A method according to any preceding claim, wherein the duration of the local exposure of the operating zone to electromagnetic radiation is controlled so as to control the spreading of the droplets on the surface, thereby controlling the resultant shape of the masking pattern.
14. A method according to any preceding claim, wherein the intensity of electromagnetic radiation is controlled so as to control the spreading of the droplets on the surface, thereby controlling the resultant shape of the masking pattern.
15. A method according to any preceding claim, wherein the operating zone extends to the surface, and local exposure of the operating zone to electromagnetic radiation is carried out subsequent to the deposition of droplets passing through the operating zone.
16. A method according to Claim 15, wherein the time period between the deposition of droplets on the surface and said local exposure is controlled so as to control spreading of the droplets on the surface.
17. A method according to Claim 16, wherein said time period is in the range from 1 to 2000 ms.
18. A method according to Claim 17, wherein said time period is in the range from 50 to 300 ms.
19. A method according to any preceding claim, wherein said electromagnetic radiation is emitted from a source integral with said deposition apparatus.
20. A method according to Claim 19, wherein said electromagnetic radiation is emitted from a plurality of sources spaced along the deposition apparatus.
21. A method according to any preceding claim, wherein the electromagnetic radiation comprises at least one of ultra violet, visible light, infra red, microwaves and alpha-particles.

**EP 1 163 552 B1**

22. A method according to any preceding claim, wherein multiple wavelengths of electromagnetic radiation are co-incident sequentially or in parallel on the deposited droplets.

23. A method according to any preceding claim, wherein the electromagnetic radiation is emitted from at least one light emitting diode.

24. A method according to Claim 23, wherein the electromagnetic radiation is emitted from an independently addressable array of light emitting diodes.

25. A method according to any of Claims 1 to 22, wherein the electromagnetic radiation is emitted from a semiconductor quantum-well solid state laser.

26. A method according to Claim 25, wherein the electromagnetic radiation is emitted from an independently addressable array of semiconductor quantum-well solid state lasers.

27. A method according to any of Claims 1 to 22, wherein the electromagnetic radiation is emitted from at least one light emitting polymer.

28. A method according to Claim 27, wherein the electromagnetic radiation emitted from said light emitting polymer is filtered to select a particular wavelength of electromagnetic radiation.

29. A method according to any of Claims 1 to 22, wherein the electromagnetic radiation is emitted from a microwave initiated gaseous discharge radiation source.

30. A method according to any of Claims 1 to 22, wherein the electromagnetic radiation is emitted from a plurality of optical fibres.

31. A method according to any preceding claim, wherein the electromagnetic radiation emitted is focused on the droplets.

32. A method according to any preceding claim, wherein, subsequent to the local exposure of the operating zone to electromagnetic radiation, the deposited masking pattern is fully exposed to electromagnetic radiation so as to ensure that the deposited droplets are cured.

33. A method according to any preceding claim, wherein the distance between the deposition apparatus and the surface is controlled during droplet deposition so as to control the time taken for a droplet to pass from the deposition apparatus on to the surface.

34. A method according to Claim 33, wherein said distance is in the range from 0.5 to 2 mm.

35. A method according to Claim 34, wherein said distance is in the range from 0.75 to 1.25 mm.

36. A method according to any preceding claim, wherein the deposited masking pattern is imaged using imaging apparatus integral with the deposition apparatus.

37. A method according to any preceding claim, comprising the step of controlling the surface energy of the surface prior to droplet deposition.

38. A method according to Claim 37, wherein the surface is subjected to at least one of abrasion, polishing, ozone treatment, plasma exposure and surface coating prior to droplet deposition.

39. A method according to any preceding claim, wherein the droplets are deposited from a droplet deposition printhead comprising a deposition chamber for housing said deposition material, an outlet nozzle in fluid communication with said deposition chamber, and means for ejecting droplets of deposition material from said deposition chamber through said outlet nozzle.

40. A method according to Claim 39, wherein the droplets are deposited from a plurality of said printheads.

## EP 1 163 552 B1

41. A method according to Claim 40, wherein the masking pattern is formed from a plurality of deposition materials, each deposition material being deposited from respective deposition printhead.
- 5 42. A method according to any of Claims 39 to 41, wherein the outlet nozzle is selectively covered to substantially prevent entry of electromagnetic radiation into the deposition printhead.
43. A method according to any of Claims 39 to 42, wherein said nozzle is cleaned after ejection of a droplet from said deposition chamber.
- 10 44. A method according to any of Claims 39 to 43, wherein said outlet nozzle is selectively covered by a nozzle shutter, said shutter comprising means for cleaning said nozzle.
45. A method according to Claim 44, wherein said outlet nozzle is cleaned by a movable wiper blade attached to said nozzle shutter.
- 15 46. A method according to Claim 44 or 45, wherein residual deposition material removed from said nozzle by said cleaning means is transferred to a reservoir housed with said deposition printhead.
47. A method according to any preceding claim, wherein the surface is disposed on a flexible sheet connected between two reels, said reels being rotated to move the surface relative to the deposition apparatus.
- 20 48. A method according to any preceding claim, comprising the step of at least partially removing said deposited masking pattern.
49. A method according to any preceding claim, wherein said masking pattern is a three-dimensional masking pattern.
- 25 50. A method according to Claim 49, wherein said masking pattern comprises a plurality of layers of deposition material, said layers being sequentially deposited on said surface.
- 30 51. A method according to Claim 50, wherein each layer has a respective shape.
52. A method according to Claim 49, wherein said masking pattern is formed from a multiplicity of droplets deposited at a plurality of deposition sites on the surface, droplets being deposited at each of said sites in turn.
- 35 53. A method according to any preceding claim, wherein said masking pattern comprises a solder reflow mask.
54. A method according to Claim 53, wherein said mask is formed from one of silicone, polyimide, polytetrafluoroethylene and epoxy.
- 40 55. A method according to any of Claims 1 to 52, wherein said masking pattern is an etching mask.
56. A method according to Claim 55, wherein said etching mask is formed from an organic-inorganic fluid.
57. A method according to Claim 55, wherein said etching mask is formed from one of epoxy, polycarbonate, silicon, polytetrafluoroethylene, polychlorotrifluoroethylene, polyimide, polyisoprene and polypropylenepolystyrene.
- 45 58. A method according to any of Claims 1 to 52, wherein said masking pattern is an electrically conductive mask.
59. A method according to Claim 58, wherein said mask is formed from one of carbon-based and metal acetate-based material.
- 50 60. A method according to any of Claims 1 to 52, wherein said masking pattern is a decorative masking pattern.
61. A method according to any of Claims 1 to 52, wherein said masking pattern is an ion implantation mask.
- 55 62. A method according to any of Claims 1 to 52, wherein said masking pattern is a confinement well mask.
63. Droplet deposition apparatus comprising a deposition chamber for housing deposition material, an outlet nozzle

in fluid communication with said deposition chamber, means for ejecting droplets of deposition material on demand from said deposition chamber through said outlet nozzle on to a surface, means for defining an operating zone through which droplets pass between the outlet nozzle and the surface, **characterized in that** said apparatus further comprises means for locally exposing the operating zone to electromagnetic radiation so as to control coalescence of droplets on the surface.

# Patentansprüche

1. Verfahren zum Ausbilden eines Markiermusters auf einer Oberfläche, wobei das Verfahren die folgenden Schritte umfasst:

die Technik eines Tropfen-Auf-Anforderung-Druckens wird verwendet, um von einem Tröpfchen-Niederschlagsapparat eine Vielzahl von Tröpfchen auf einer Oberfläche niederzuschlagen, um ein Maskiermuster auszubilden wobei die Tröpfchen durch einen Betriebsbereich hindurchgelangen der zwischen dem Niederschlagsapparat und der Oberfläche liegt, dadurch gekennzeichnet, dass das Verfahren weiter den Schritt umfasst, wonach lokal der Betriebsbereich elektromagnetischer Strahlung ausgesetzt wird, umso ein Zusammenwachsen von Tröpfchen auf der Oberfläche zu steuern, wobei dadurch die Festigkeit des Maskiermusters gesteuert wird.

2. Verfahren nach Anspruch 1, bei welchem die Ausbildung des Maskiermusters so gesteuert wird, dass das Maskiermuster vorbestimmte strukturelle Eigenschaften hat.

3. Verfahren nach Anspruch 1 oder 2, bei welchem der Betriebsbereich sich von dem Niederschlagsapparat zu der Oberfläche erstreckt.

4. Verfahren nach einem der vorhergehenden Ansprüche, bei welchem eine relative Bewegung zwischen dem Abscheideapparat und der Oberfläche so bewirkt wird, dass der Betriebsbereich sich über die Oberfläche während einer Ausbildung des Maskiermusters bewegt.

5. Verfahren nach einem vorhergehenden Anspruch, bei welchem die lokale Umgebung des Betriebsbereichs so gesteuert wird, dass das Zusammenwachsen der Tröpfchen auf der Oberfläche gesteuert wird.

6. Verfahren nach einem der vorhergehenden Ansprüche, bei welchem die lokale Umgebung des Betriebsbereichs gesteuert wird, dass die Ausbreitung der Tröpfchen auf der Oberfläche gesteuert wird.

7. Verfahren nach einem vorhergehenden Anspruch, bei welchem die lokale Umgebung des Betriebsbereichs so gesteuert wird, dass eine Platzierung der Tröpfchen auf der Oberfläche gesteuert wird.

8. Verfahren nach einem vorhergehenden Anspruch, bei welchem die lokale Temperatur des Betriebsbereichs so gesteuert wird, dass die Rate der Verfestigung der Tröpfchen auf der Oberfläche gesteuert wird.

9. Verfahren nach einem vorhergehenden Anspruch, bei welchem die lokale Atmosphäre des Betriebsbereichs gesteuert wird.

10. Verfahren nach Anspruch 9, bei welchem wenigstens ein Teilvakuum in dem Betriebsbereich gesteuert wird, umso im wesentlichen eine Verschmutzung der Tröpfchen während eines Durchgangs von dem Niederschlagsapparat zu der Oberfläche zu vermeiden.

11. Verfahren nach Anspruch 9 oder 10, bei welchem ein Druckdifferenzial das sich zwischen dem Niederschlagsapparat und der Oberfläche erstreckt, in dem Betriebsbereich ausgebildet ist.

12. Verfahren nach einem der Ansprüche 9 bis 11, bei welchem ein träges oder reaktives Gas in den Betriebsbereich während eines Tröpfchenniederschlags eingeführt wird.

13. Verfahren nach einem der vorhergehenden Ansprüche, bei welchem die Dauer, während der der Betriebsbereich einer elektromagnetischer Strahlung ausgesetzt ist, gesteuert wird, umso die Ausbreitung der Tröpfchen auf der Oberfläche zu steuern, wobei dadurch die sich ergebende Form des Maskiermusters gesteuert wird.

## EP 1 163 552 B1

14. Verfahren nach einem vorhergehenden Anspruch, bei welchem die Intensität einer elektromagnetischen Strahlung gesteuert wird, umso das Ausbreiten der Tröpfchen auf der Oberfläche zu steuern, wobei dadurch die sich ergebende Gestalt des Maskiermusters gesteuert wird.

5 15. Verfahren nach einem vorhergehenden Anspruch, bei welchem sich der Betriebsbereich zu der Oberfläche erstreckt und der Betriebsbereich lokal einer elektromagnetischen Strahlung ausgesetzt wird, und zwar nachfolgend zu den Niederschlag von Tröpfchen, die durch den Betriebsbereich hindurchgelangen.

10 16. Verfahren nach Anspruch 15, bei welchem die Zeitdauer zwischen dem Niederschlag von Tröpfchen auf der Oberfläche und dem lokalen Aussetzen gesteuert wird, umso ein Ausbreiten der Tröpfchen auf der Oberfläche zu steuern.

17. Verfahren nach Anspruch 16, bei welchem die Zeitdauer in dem Bereich von 1000 bis 2000 ms liegt.

15 18. Verfahren nach Anspruch 17, bei welchem die Zeitdauer in dem Bereich von 50 bis 300 ms liegt.

19. Verfahren nach einem vorhergehenden Anspruch, bei welchem die elektromagnetische Strahlung von einer Quelle emittiert wird, die mit dem Niederschlagsapparat einstückig ist.

20 20. Verfahren nach Anspruch 19, bei welchem die elektromagnetische Strahlung von einer Vielzahl von Quellen emittiert wird, die entlang des Niederschlagsapparats beabstandet sind.

21. Verfahren nach einem vorhergehenden Anspruch, bei welchem die elektromagnetische Strahlung wenigstens eine der folgenden umfasst:

25 Ultraviolett, sichtbar als Licht, Infrarot, Mikrowellen und Alfateilchen

30 22. Verfahren nach einem der vorhergehenden Ansprüche, bei welchem mehrere Wellenlängen der elektromagnetischen Strahlung sequenziell koinzident sind oder parallel auf den niedergeschlagenen Tröpfchen.

23. Verfahren nach einem vorhergehenden Anspruch, bei welchem die elektromagnetische Strahlung aus wenigstens einer Lichtemissionsdiode emittiert wird.

35 24. Verfahren nach Anspruch 23, bei welchem die elektromagnetische Strahlung von einem unabhängig adressierbaren Array von Lichtemissionsdioden emittiert wird.

25. Verfahren nach einem der Ansprüche 1 bis 22, bei welchem die elektromagnetische Strahlung von einem Halbleiter-Quantum-Well-Festkörperlaser emittiert wird.

40 26. Verfahren nach Anspruch 25, bei welchem die elektromagnetische Strahlung von einem unabhängig adressierbar Array von Halbleiter-Quantum-Well-Festkörperlaser emittiert wird.

45 27. Verfahren nach einem der Ansprüche 1 bis 22, bei welchem die elektromagnetische Strahlung von wenigstens einem Lichtemissionspolymer emittiert wird.

28. Verfahren nach Anspruch 27, bei welchem die elektromagnetische Strahlung, die von den Lichtemissionspolymer emittiert wird, gefiltert wird, um eine bestimmte Wellenlänge elektromagnetischer Strahlung auszuwählen.

50 29. Verfahren nach einem der Ansprüche 1 bis 22, bei welchem die elektromagnetische Strahlung von einer Mikrowellen-initiierten bzw. gezündeten Gas-Entladungs-Strahlungsquelle emittiert wird.

30. Verfahren nach einem der Ansprüche 1 bis 22, bei welchem die elektromagnetische Strahlung von einer Vielzahl von optischen Fasern emittiert wird.

55 31. Verfahren nach einem der vorhergehenden Ansprüche, bei welchem die elektromagnetische Strahlung, die emittiert wird, auf die Tröpfchen fokussiert ist.

32. Verfahren nach einem vorhergehenden Anspruch, bei dem, nachdem der Betriebsbereich einer elektromagnetischen



schen Strahlung ausgesetzt wurde, das niedergeschlagene bzw. abgeschiedene Maskiermuster vollständig der elektromagnetischen Strahlung ausgesetzt wird, umso zu gewährleisten, dass die niedergeschlagenen Tröpfchen ausgehärtet werden.

- 5 33. Verfahren nach einem vorhergehenden Anspruch, bei welchem der Abstand zwischen dem Abscheideapparat und der Oberfläche während eines Tröpfchenniederschlags gesteuert wird, umso die Zeit zu steuern, die ein Tröpfchen braucht, um von dem Niederschlagsapparat auf die Oberfläche zu gelangen.
- 10 34. Verfahren nach Anspruch 33, bei welchem der Abstand in dem Bereich von 0,5 bis 2 mm liegt.
35. Verfahren nach Anspruch 34, bei welchem der Abstand im Bereich von 0,75 bis 1,25 mm liegt.
- 15 36. Verfahren nach einem vorhergehenden Anspruch, bei welchem das abgeschiedene Maskiermuster unter Verwendung eines Abbildungsapparats abgebildet wird, der mit dem Abscheideapparat einstückig ist.
37. Verfahren nach einem vorhergehenden Anspruch, dass den Schritt umfasst, wonach die Oberflächenenergie der Oberfläche vor der Tröpfchenabscheidung gesteuert wird.
- 20 38. Verfahren nach Anspruch 37, bei welchem die Oberfläche wenigstens einem der folgenden Ansprüche ausgesetzt wird:  
  
Abrasion, Polieren, Ozonbehandlung, Plasma-Aussetzen bzw. Plasma-Behandlung und Oberflächenbeschichtung, und zwar vor der Tröpfchenabscheidung bzw. vor dem Tröpfchenniederschlag
- 25 39. Verfahren nach einem vorhergehenden Anspruch, bei welchem die Tröpfchen von einem Tröpfchenniederschlags-Druckkopf niedergeschlagen werden, der umfasst eine Niederschlagskammer zum aufnehmen des Niederschlagsmaterials, eine Ausgangsdüse in Fluidkommunikation mit der Niederschlagskammer und ein Mittel zum Ausstoßen von Tröpfchen von Niederschlagsmaterial von der Niederschlagskammer durch die Auslassdüse.
- 30 40. Verfahren nach Anspruch 39, bei welchem die Tröpfchen von einer Vielzahl der Druckköpfe niedergeschlagen werden.
41. Verfahren nach Anspruch 40, bei welchem das Maskiermuster aus einer Vielzahl von Niederschlagsmaterialien ausgebildet ist, wobei jedes Niederschlagsmaterial von einem jeweiligen Niederschlags-Druckkopf niedergeschlagen wird.
- 35 42. Verfahren nach einem der Ansprüche 39 bis 41, bei welchem die Auslassdüse selektiv abgedeckt wird um einen Eintritt elektromagnetischer Strahlen in den Niederschlags-Druckkopf im Wesentlichen zu verhindern.
- 40 43. Verfahren nach einem der Ansprüche 39 bis 42, bei welchem die Düse nach Ausstoßen eines Tröpfchens von der Niederschlagskammer gereinigt wird.
44. Verfahren nach einem der Ansprüche 39 bis 43, bei welchem die Auslassdüse selektiv durch einen Düsenverschluss abgedeckt wird, wobei der Verschluss ein Mittel umfasst, um die Düse zu reinigen.
- 45 45. Verfahren nach Anspruch 44, bei welchem die Auslassdüse von einer beweglichen Wischklinge gereinigt wird, die an den Düsenverschluss angebracht wird.
- 50 46. Verfahren nach Anspruch 44 oder 45, bei welchem ein Restabscheidematerial, das von der Düse durch das Reinigungsmittel entfernt wird, zu einem Reservoir übertragen wird, das mit dem Niederschlagsdruckkopf untergebracht ist.
47. Verfahren nach einem vorhergehenden Anspruch, bei welchem die Oberfläche auf einem flexiblen Platz angeordnet ist, dass zwischen zwei Rollen bzw. Spulen eine Verbindung herstellt, wobei die Rollen bzw. Spulen gedreht werden, um die Oberfläche zu den Niederschlagsapparat zu bewegen.
- 55 48. Verfahren nach einem vorhergehenden Anspruch, dass den Schritt umfasst, wonach wenigstens teilweise das Niederschlags-Maskiermuster entfernt wird.

## EP 1 163 552 B1

49. Verfahren nach einem vorhergehenden Anspruch, bei welchem das Maskiermuster ein dreidimensionales Maskiermuster ist.

50. Verfahren nach Anspruch 49, bei welchem das Maskiermuster eine Vielzahl von Schichten von Niederschlagsmaterial umfasst, wobei die Schichten sequenziell auf der Oberfläche niedergeschlagen werden.

51. Verfahren nach Anspruch 50, bei welchem jede Schicht eine entsprechende Gestalt hat.

52. Verfahren nach Anspruch 49, bei welchem das Maskiermuster aus einer Mehrzahl bzw. Vielzahl von Tröpfchen ausgebildet ist, die auf einer Vielzahl von Niederschlagswellen auf der Oberfläche abgeschieden werden, wobei Tröpfchen bei jeder der Stellen der Reihe nach bzw. abwechselnd abgeschieden werden.

53. Verfahren nach einem vorhergehenden Anspruch, bei welchem das Maskiermuster eine Lötmittel-Rückflussmaske umfasst.

54. Verfahren nach Anspruch 53, bei welchem die Maske aus einem der folgenden ausgebildet ist:

Silikon, Polyamid, Polytetrafluorethylen und Epoxy.

55. Verfahren nach einem der Ansprüche 1 bis 51, bei welchem das Maskiermuster eine Ätzmase ist.

56. Verfahren nach Anspruch 55, bei welchem die Ätzmase aus einem organischinorganisch-Fluid ausgebildet ist.

57. Verfahren nach Anspruch 55, bei welchem die Ätzmase aus einem der folgenden ausgebildet ist:

Epoxy, Polycarbonat, Silizium, Polytetrafluorethylen, Polychlortrifluorethylen, Polyimid, Polyisopren, Polypropylenpolystyren.

58. Verfahren nach einem der Ansprüche 1 bis 52, bei welchem das Maskiermuster eine elektrisch leitende Maske ist.

59. Verfahren nach Anspruch 58, bei welchem die Maske aus einem der folgenden ausgebildet ist:  
kunststoffbasiertes und metallazetat-basiertes Material.

60. Verfahren nach einem der Ansprüche 1 bis 52, bei welchem das Maskiermuster ein Ziermaskiermuster ist.

61. Verfahren nach einem der Ansprüche 1 bis 53, bei welchem das Maskiermuster eine Ionenimplantationsmaske ist.

62. Verfahren nach einem der Ansprüche 1 bis 52, bei welchem das Maskiermuster eine Confinement-Well- bzw. Einsperrungs-Loch-Maske ist.

63. Tröpfchen-Niederschlagsapparat, der umfasst eine Niederschlagskammer zum Aufnehmen von Niederschlagsmaterial, eine Auslassdüse in Fluidkommunikation mit der Niederschlagskammer, ein Mittel zum Ausstoßen von Tröpfchen von Niederschlagsmaterial auf Anforderung von der Niederschlagskammer durch die Auslassdüse auf eine Oberfläche, ein Mittel zum Festlegen eines Betriebsbereichs durch den Tröpfchen zwischen der Auslassdüse und der Oberfläche hindurch gelangen, **dadurch gekennzeichnet, dass** der Apparat weiter umfasst ein Mittel, um den Betriebsbereich lokal einer elektromagnetischen Strahlung auszusetzen, umso ein Zusammenwaschen von Tröpfchen auf der Oberfläche zu steuern.

## Revendications

1. Un procédé de formation d'un motif de masquage sur une surface, ce procédé comprenant l'étape suivante :

on utilise la technique d'impression par goutte à la demande pour déposer à partir d'un appareil de dépôt de gouttelettes une multiplicité de gouttelettes sur une surface pour former un motif de masquage, ces gouttelettes traversant une zone d'action située entre l'appareil de dépôt et la surface, **caractérisé en ce que** ce procédé comprend en outre l'étape suivante  
on expose localement la zone d'action à un rayonnement électromagnétique de façon à commander la coa-

lescence de gouttelettes sur la surface, pour commander ainsi la continuité du motif de masquage.

2. Un procédé selon la revendication 1, dans lequel la formation du motif de masquage est commandée de façon que le motif de masquage ait des propriétés structurales prédéterminées.
- 5 3. Un procédé selon la revendication 1 ou 2, dans lequel la zone d'action s'étend à partir de l'appareil de dépôt jusqu'à la surface.
- 10 4. Un procédé selon l'une quelconque des revendications précédentes, dans lequel un mouvement relatif est effectué entre l'appareil de dépôt et la surface de façon à déplacer la zone d'action sur l'étendue de la surface pendant la formation du motif de masquage.
- 15 5. Un procédé selon l'une quelconque des revendications précédentes, dans lequel l'environnement local de la zone d'action est commandé de façon à commander la coalescence des gouttelettes sur la surface.
6. Un procédé selon l'une quelconque des revendications précédentes, dans lequel l'environnement local de la zone d'action est commandé de façon à commander l'étalement des gouttelettes sur la surface.
- 20 7. Un procédé selon l'une quelconque des revendications précédentes, dans lequel l'environnement local de la zone d'action est commandé de façon à commander le placement des gouttelettes sur la surface.
8. Un procédé selon l'une quelconque des revendications précédentes, dans lequel la température locale de la zone d'action est commandée de façon à commander la vitesse de solidification des gouttelettes sur la surface.
- 25 9. Un procédé selon l'une quelconque des revendications précédentes, dans lequel l'atmosphère locale de la zone d'action est commandée.
- 30 10. Un procédé selon la revendication 9, dans lequel un vide au moins partiel est établi dans la zone d'action, de façon à éviter pratiquement une contamination des gouttelettes pendant le passage à partir de l'appareil de dépôt jusqu'à la surface.
11. Un procédé selon la revendication 9 ou 10, dans lequel une différence de pression s'étendant entre l'appareil de dépôt et la surface est établie dans la zone d'action.
- 35 12. Un procédé selon l'une quelconque des revendications 9 à 11, dans lequel un gaz inerte ou réactif est introduit dans la zone d'action pendant le dépôt de gouttelettes.
13. Un procédé selon l'une quelconque des revendications précédentes, dans lequel la durée de l'exposition locale de la zone d'action au rayonnement électromagnétique est commandée de façon à commander l'étalement des gouttelettes sur la surface, pour commander ainsi la forme résultante du motif de masquage.
- 40 14. Un procédé selon l'une quelconque des revendications précédentes, dans lequel l'intensité du rayonnement électromagnétique est commandée de façon à commander l'étalement des gouttelettes sur la surface, pour commander ainsi la forme résultante du motif de masquage.
- 45 15. Un procédé selon l'une quelconque des revendications précédentes, dans lequel la zone d'action s'étend jusqu'à la surface, et l'exposition locale de la zone d'action au rayonnement électromagnétique est accomplie à la suite du dépôt de gouttelettes passant à travers la zone d'action.
- 50 16. Un procédé selon la revendication 15, dans lequel l'intervalle de temps entre le dépôt de gouttelettes sur la surface et l'exposition locale est commandé de façon à commander l'étalement des gouttelettes sur la surface.
17. Un procédé selon la revendication 16, dans lequel l'intervalle de temps est dans la plage de 1 à 200 ms.
- 55 18. Un procédé selon la revendication 17, dans lequel l'intervalle de temps est dans la plage de 50 à 300 ms.
19. Un procédé selon l'une quelconque des revendications précédentes, dans lequel le rayonnement électromagnétique est émis par une source intégrée à l'appareil de dépôt.

## EP 1 163 552 B1

20. Un procédé selon la revendication 19, dans lequel le rayonnement électromagnétique est émis par une multiplicité de sources espacées le long de l'appareil de dépôt.
- 5 21. Un procédé selon l'une quelconque des revendications précédentes, dans lequel le rayonnement électromagnétique comprend l'un au moins des suivants : ultraviolet, lumière visible, infrarouge, micro-ondes et particules alpha.
22. Un procédé selon l'une quelconque des revendications précédentes, dans lequel de multiples longueurs d'onde de rayonnement électromagnétique tombent conjointement, séquentiellement ou en parallèle, sur les gouttelettes déposées.
- 10 23. Un procédé selon l'une quelconque des revendications précédentes, dans lequel le rayonnement électromagnétique est émis par au moins une diode électroluminescente.
24. Un procédé selon la revendication 23, dans lequel le rayonnement électromagnétique est émis par un réseau de diodes électroluminescentes pouvant être adressées indépendamment.
- 15 25. Un procédé selon l'une quelconque des revendications 1 à 22, dans lequel le rayonnement électromagnétique est émis par un laser à l'état solide à puits quantique à semiconducteur.
- 20 26. Un procédé selon la revendication 25, dans lequel le rayonnement électromagnétique est émis par un réseau de lasers à l'état solide à puits quantique à semiconducteur pouvant être adressés indépendamment.
27. Un procédé selon l'une quelconque des revendications 1 à 22, dans lequel le rayonnement électromagnétique est émis par au moins un polymère électroluminescent.
- 25 28. Un procédé selon la revendication 27, dans lequel le rayonnement électromagnétique émis par le polymère électroluminescent est filtré pour sélectionner une longueur d'onde particulière de rayonnement électromagnétique.
29. Un procédé selon l'une quelconque des revendications 1 à 22, dans lequel le rayonnement électromagnétique est émis par une source de rayonnement à décharge dans un gaz déclenchée par micro-ondes.
- 30 30. Un procédé selon l'une quelconque des revendications 1 à 22, dans lequel le rayonnement électromagnétique est émis par une multiplicité de fibres optiques.
- 35 31. Un procédé selon l'une quelconque des revendications précédentes, dans lequel le rayonnement électromagnétique émis est focalisé sur les gouttelettes.
32. Un procédé selon l'une quelconque des revendications précédentes, dans lequel, à la suite de l'exposition locale de la zone d'action au rayonnement électromagnétique, le motif de masquage déposé est complètement exposé à un rayonnement électromagnétique pour faire en sorte que les gouttelettes déposées subissent une maturation.
- 40 33. Un procédé selon l'une quelconque des revendications précédentes, dans lequel la distance entre l'appareil de dépôt et la surface est commandée pendant le dépôt de gouttelettes de façon à commander le temps que met une gouttelette pour passer de l'appareil de dépôt à la surface.
- 45 34. Un procédé selon la revendication 33, dans lequel la distance est dans la plage de 0,5 à 2 mm.
35. Un procédé selon la revendication 34, dans lequel la distance est dans la plage de 0,75 à 1,25 mm.
- 50 36. Un procédé selon l'une quelconque des revendications précédentes, dans lequel on forme une image avec le motif de masquage déposé, en utilisant un appareil de formation d'image intégré à l'appareil de dépôt.
37. Un procédé selon l'une quelconque des revendications précédentes, comprenant l'étape consistant à commander l'énergie superficielle de la surface avant le dépôt de gouttelettes.
- 55 38. Un procédé selon la revendication 37, dans lequel la surface est soumise à au moins une opération parmi l'abrasion, le polissage, le traitement à l'ozone, l'exposition par plasma et le revêtement de surface, avant le dépôt de gouttelettes.

## EP 1 163 552 B1

- 5 39. Un procédé selon l'une quelconque des revendications précédentes, dans lequel les gouttelettes sont déposées à partir d'une tête d'impression à dépôt de gouttelettes comprenant une chambre de dépôt pour contenir la matière de dépôt, une buse de sortie en communication pour le fluide avec la chambre de dépôt, et un moyen pour éjecter des gouttelettes de la matière de dépôt à partir de la chambre de dépôt, à travers la buse de sortie.
40. Un procédé selon la revendication 39, dans lequel les gouttelettes sont déposées à partir d'une multiplicité des têtes d'impression.
- 10 41. Un procédé selon la revendication 40, dans lequel le motif de masquage est formé à partir d'une multiplicité de matières de dépôt, chaque matière de dépôt étant déposée à partir d'une tête de dépôt respective.
42. Un procédé selon l'une quelconque des revendications 39 à 41, dans lequel la buse de sortie est sélectivement recouverte pour empêcher pratiquement l'entrée de rayonnement électromagnétique à l'intérieur de la tête d'impression par dépôt.
- 15 43. Un procédé selon l'une quelconque des revendications 39 à 42, dans lequel la buse est nettoyée après l'éjection d'une gouttelette à partir de la chambre de dépôt.
44. Un procédé selon l'une quelconque des revendications 39 à 43, dans lequel la buse de sortie est couverte sélectivement par un obturateur de buse, cet obturateur comprenant des moyens pour nettoyer la buse.
- 20 45. Un procédé selon la revendication 44, dans lequel la buse de sortie est nettoyée par une raclette d'essuyage mobile fixée à l'obturateur de buse.
- 25 46. Un procédé selon la revendication 44 ou 45, dans lequel la matière de dépôt résiduelle enlevée de la buse par les moyens de nettoyage est transférée vers un réservoir logé à l'intérieur de la tête d'impression par dépôt.
- 30 47. Un procédé selon l'une quelconque des revendications précédentes, dans lequel la surface est disposée sur une feuille flexible s'étendant entre deux bobines, ces bobines étant mises en rotation pour déplacer la surface par rapport à l'appareil de dépôt.
48. Un procédé selon l'une quelconque des revendications précédentes, comprenant l'étape consistant à enlever au moins partiellement le motif de masquage déposé.
- 35 49. Un procédé selon l'une quelconque des revendications précédentes, dans lequel le motif de masquage est un motif de masquage tridimensionnel.
50. Un procédé selon la revendication 49, dans lequel le motif de masquage comprend une multiplicité de couches de matière de dépôt, ces couches étant déposées séquentiellement sur la surface.
- 40 51. Un procédé selon la revendication 50, dans lequel chaque couche a une forme respective.
52. Un procédé selon la revendication 49, dans lequel le motif de masquage est formé à partir d'une multiplicité de gouttelettes déposées à une multiplicité de sites de dépôt sur la surface, des gouttelettes étant déposées tour à tour à chacun des sites.
- 45 53. Un procédé selon l'une quelconque des revendications précédentes, dans lequel le motif de masquage est un masque de refusion de brasure.
- 50 54. Un procédé selon la revendication 53, dans lequel le masque est formé à partir de l'une des matières suivantes : silicone, polyimide, polytétrafluoroéthylène et époxy.
- 55 55. Un procédé selon l'une quelconque des revendications 1 à 52, dans lequel le motif de masquage est un masque de gravure.
56. Un procédé selon la revendication 55, dans lequel le masque de gravure est formé à partir d'un fluide organique-inorganique.

## EP 1 163 552 B1

57. Un procédé selon la revendication 55, dans lequel le masque de gravure est formé à partir de l'une des matières suivantes :

5                   époxy, polycarbonate, silicone, polytétrafluoroéthylène, polychlorotrifluoroéthylène, polyimide, polyisoprène et polypropylène polystyrène.

58. Un procédé selon l'une quelconque des revendications 1 à 52, dans lequel le motif de masquage est un masque électriquement conducteur.

10 59. Un procédé selon la revendication 58, dans lequel le masque est formé à partir de l'une d'une matière à base de carbone et d'une matière à base d'acétate de métal.

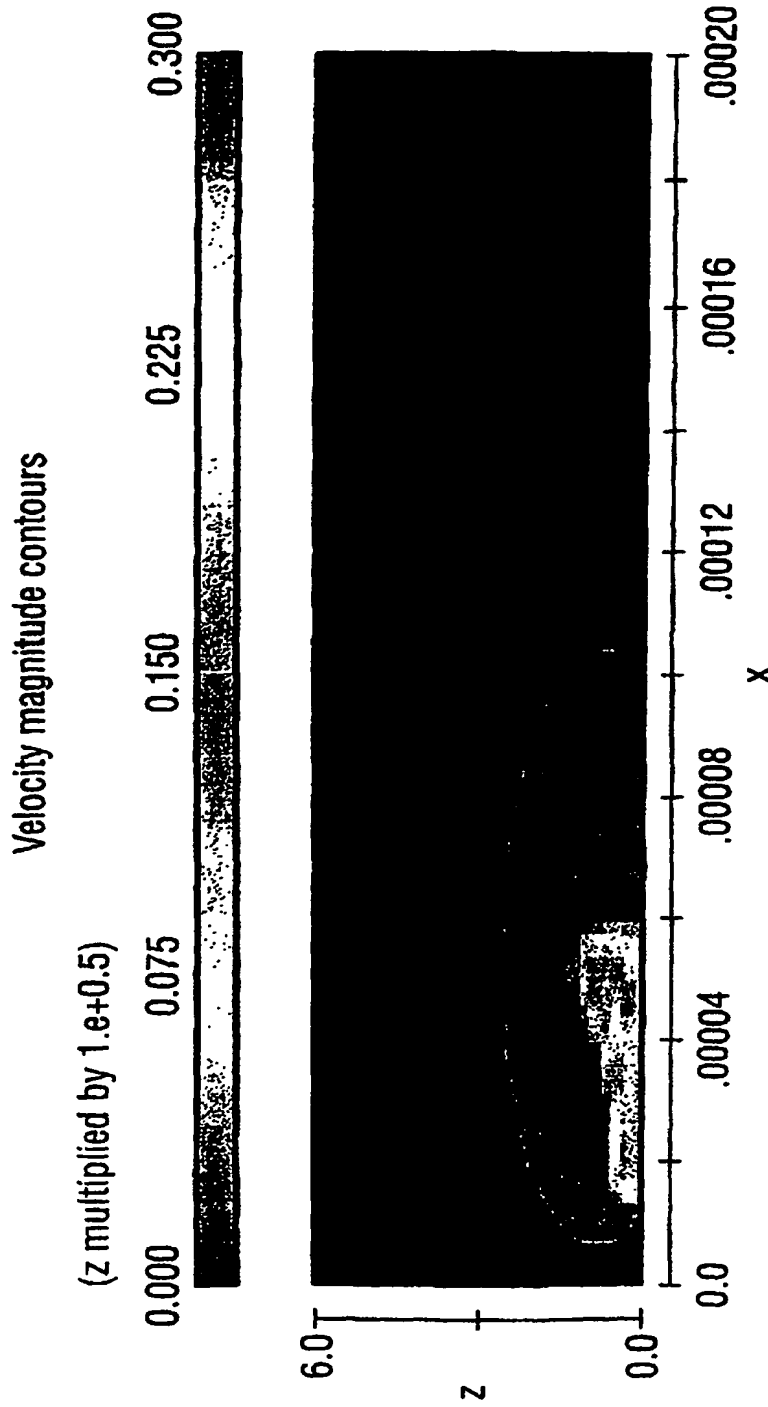
60. Un procédé selon l'une quelconque des revendications 1 à 52, dans lequel le motif de masquage est un motif de masquage décoratif.

15 61. Un procédé selon l'une quelconque des revendications 1 à 52, dans lequel le motif de masquage est un masque d'implantation ionique.

20 62. Un procédé selon l'une quelconque des revendications 1 à 52, dans lequel le motif de masquage est un masque de puits de confinement.

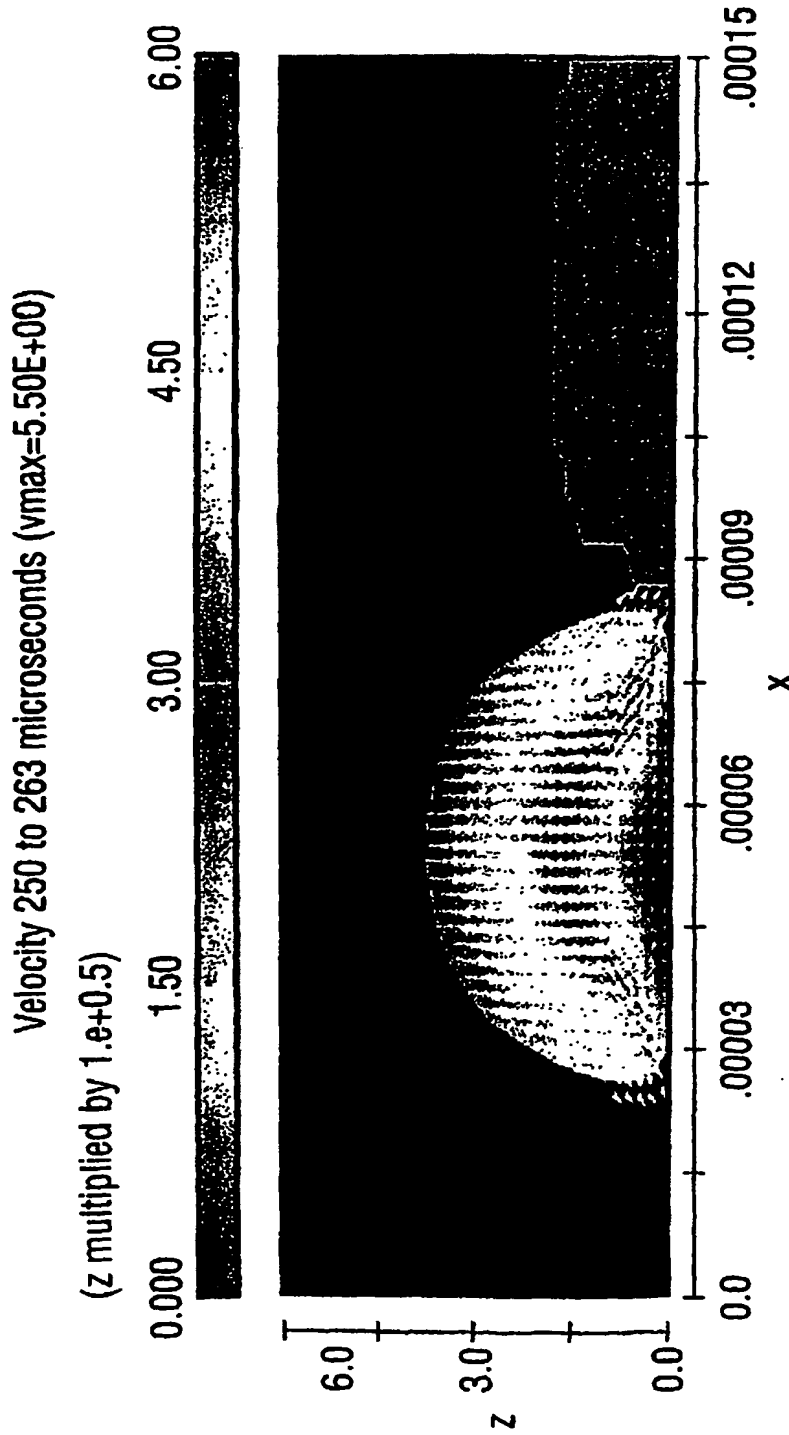
25 63. Appareil de dépôt de gouttelettes comprenant une chambre de dépôt pour contenir une matière de dépôt, une buse de sortie en communication pour le fluide avec la chambre de dépôt, des moyens pour éjecter des gouttelettes de matière de dépôt, à la demande, à partir de la chambre de dépôt, à travers la buse de sortie, pour qu'elles atteignent une surface, des moyens pour définir une zone d'action à travers laquelle des gouttelettes passent entre la buse de sortie et la surface, **caractérisé en ce que** cet appareil comprend en outre des moyens pour exposer localement la zone d'action à un rayonnement électromagnétique, de façon à commander la coalescence de gouttelettes sur la surface.

FIG. 1



Flow-3D t=9.9988E-06 y=5.000E-01 (ix=2 to 101 kz=2 to 31)  
 17:56:04 2-9-1999eifd hydr3D: version 7.1.5 win 32 1998  
 51.1 dia : 000 to 250 microseconds

**FIG. 2a**



Flow-3D t=3.0000E-06 y=1.000E-06 (ix=2 to 76 kz=2 to 31)  
 17:30:04 2-17-1999eifd hydr3D: version 7.1.5 win 32 1998  
 51.1 dia : Fluid droplet impact with solidified droplet 3D



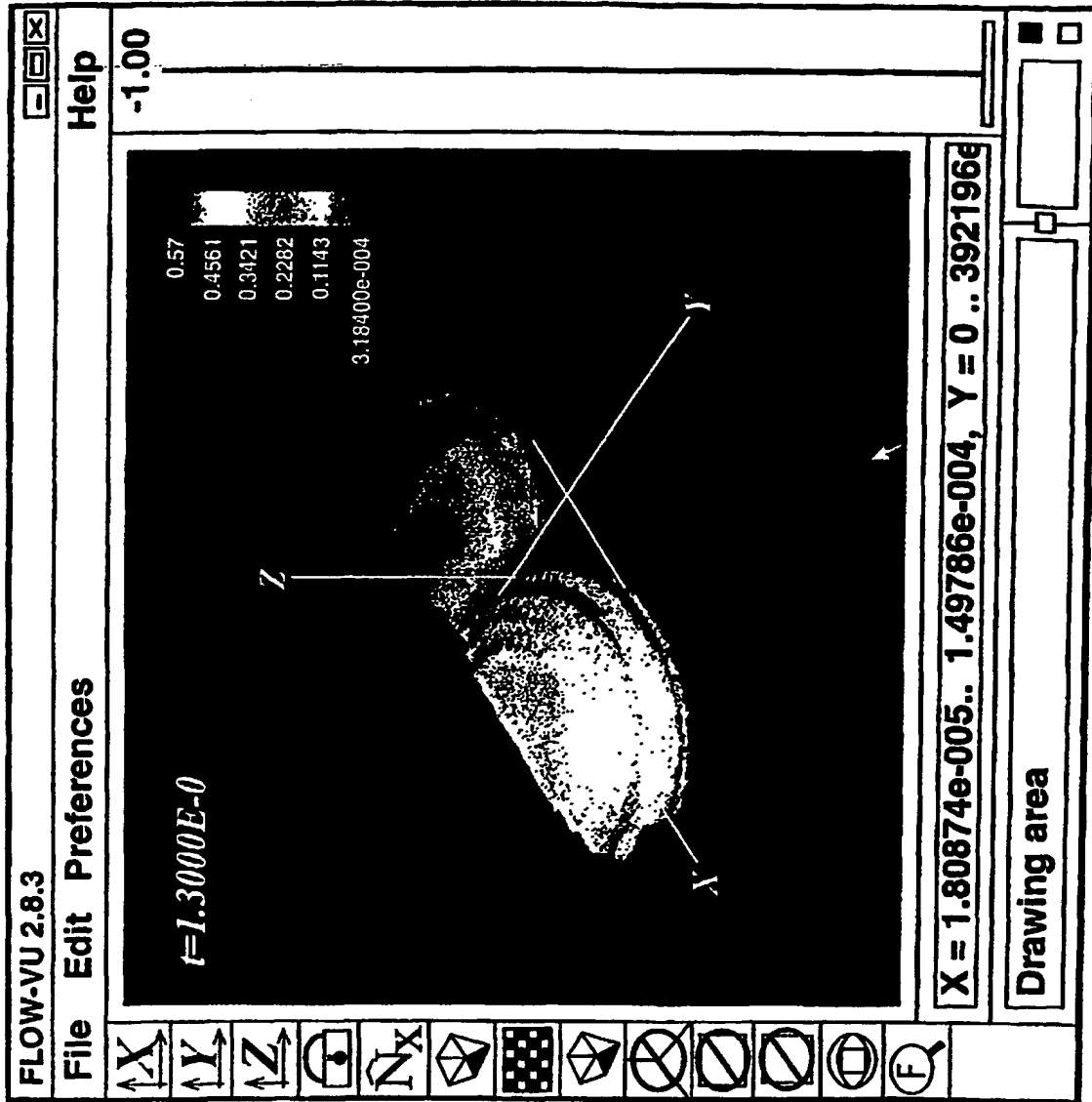
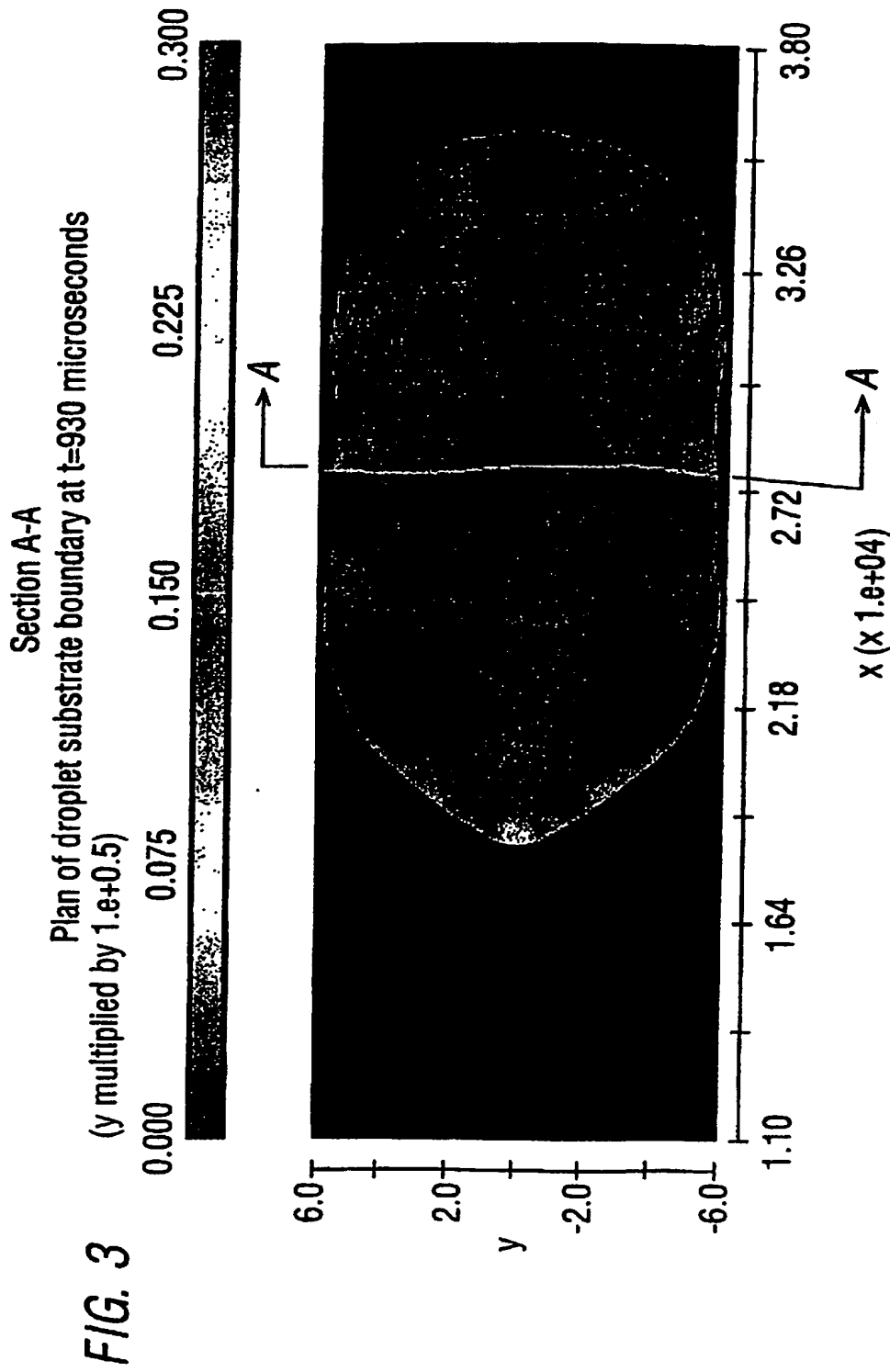
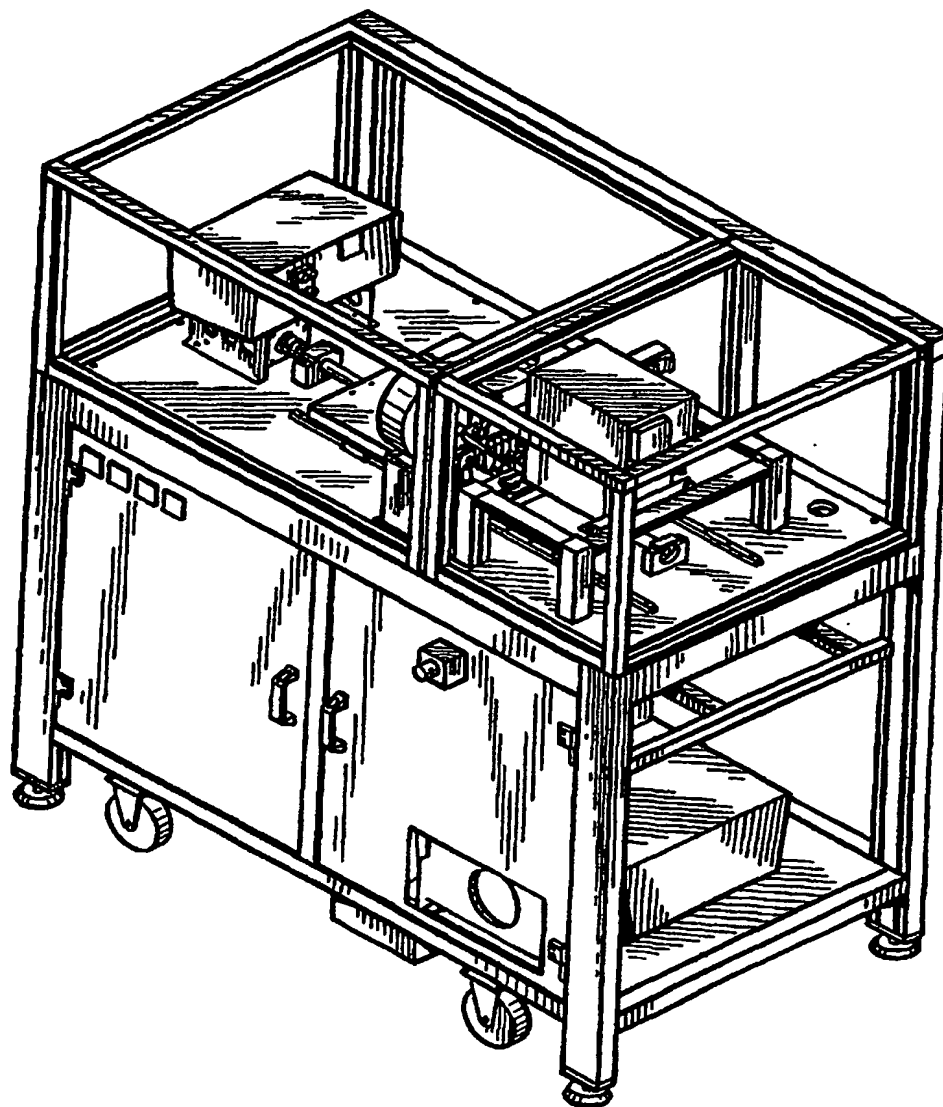


FIG. 2b



Flow-3D  $t=6.809E-04$   $z=1.000E-06$  ( $ix=2$  to  $136$   $jy=2$  to  $31$ )  
 20:04:05 2-17-1999eifd hydr3D: version 7.1.5 win 32 1998  
 51.1 dia : 675 to 975 microseconds - 3D droplets

*FIG. 4*



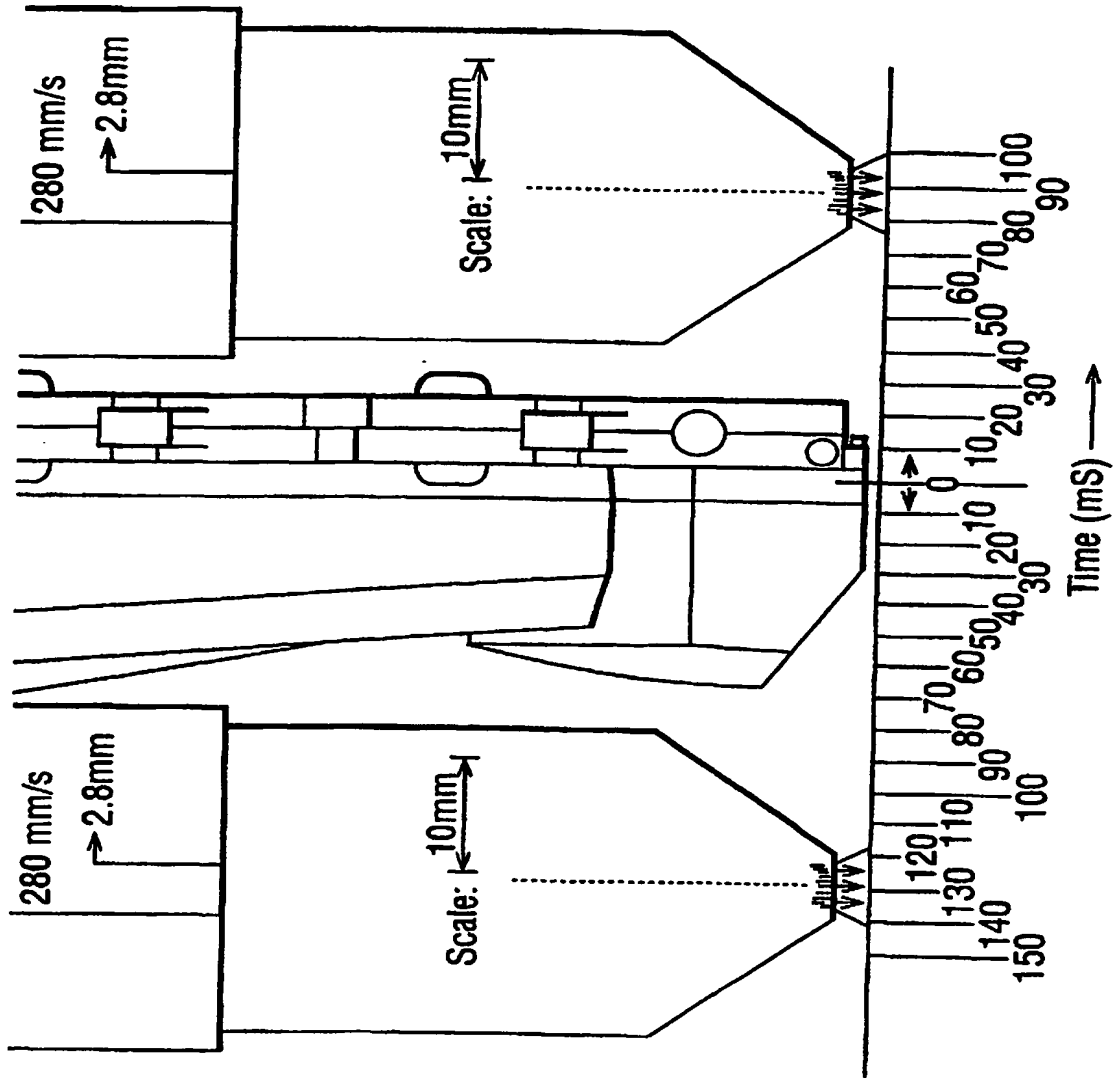
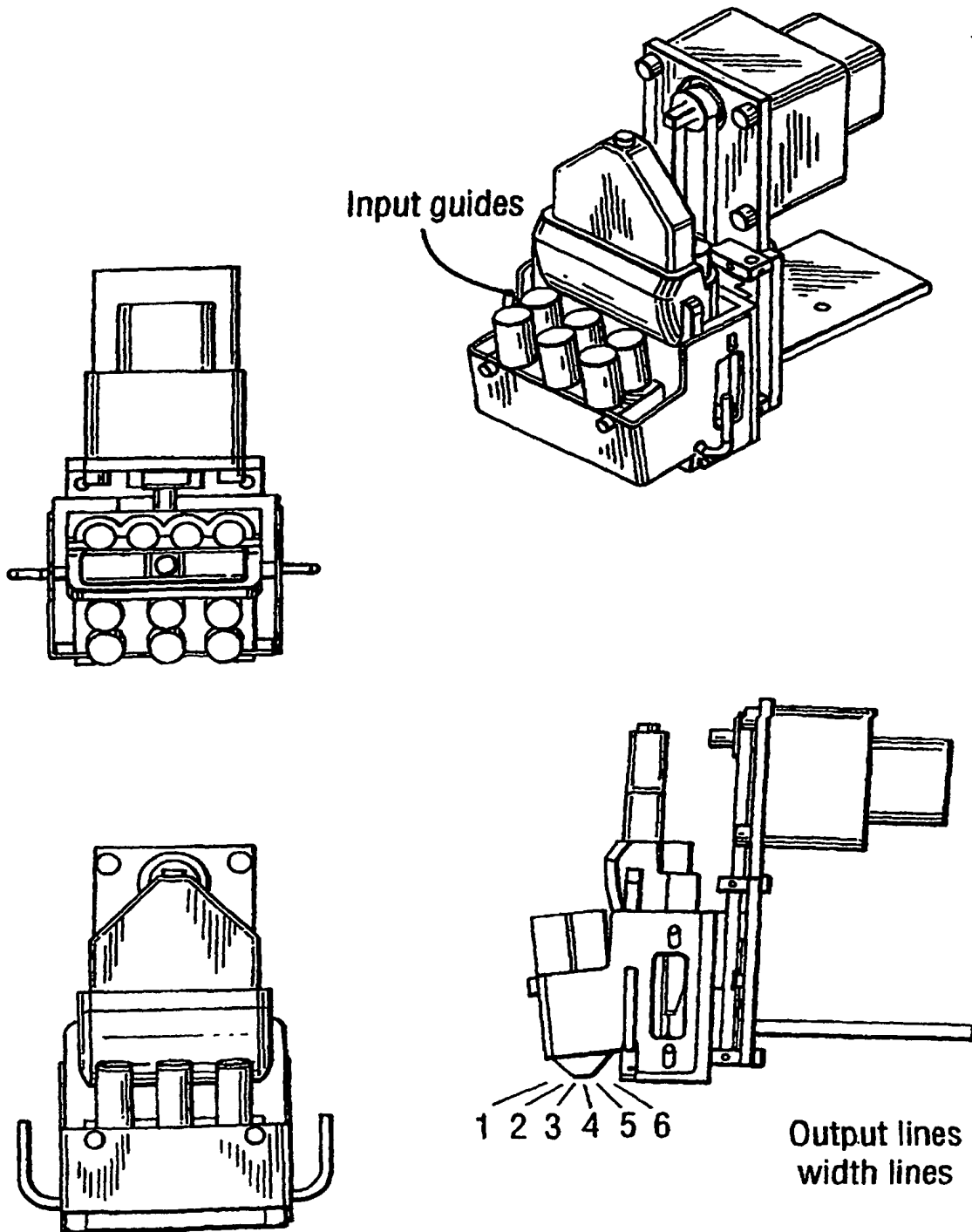


FIG. 5a

*FIG. 5b*



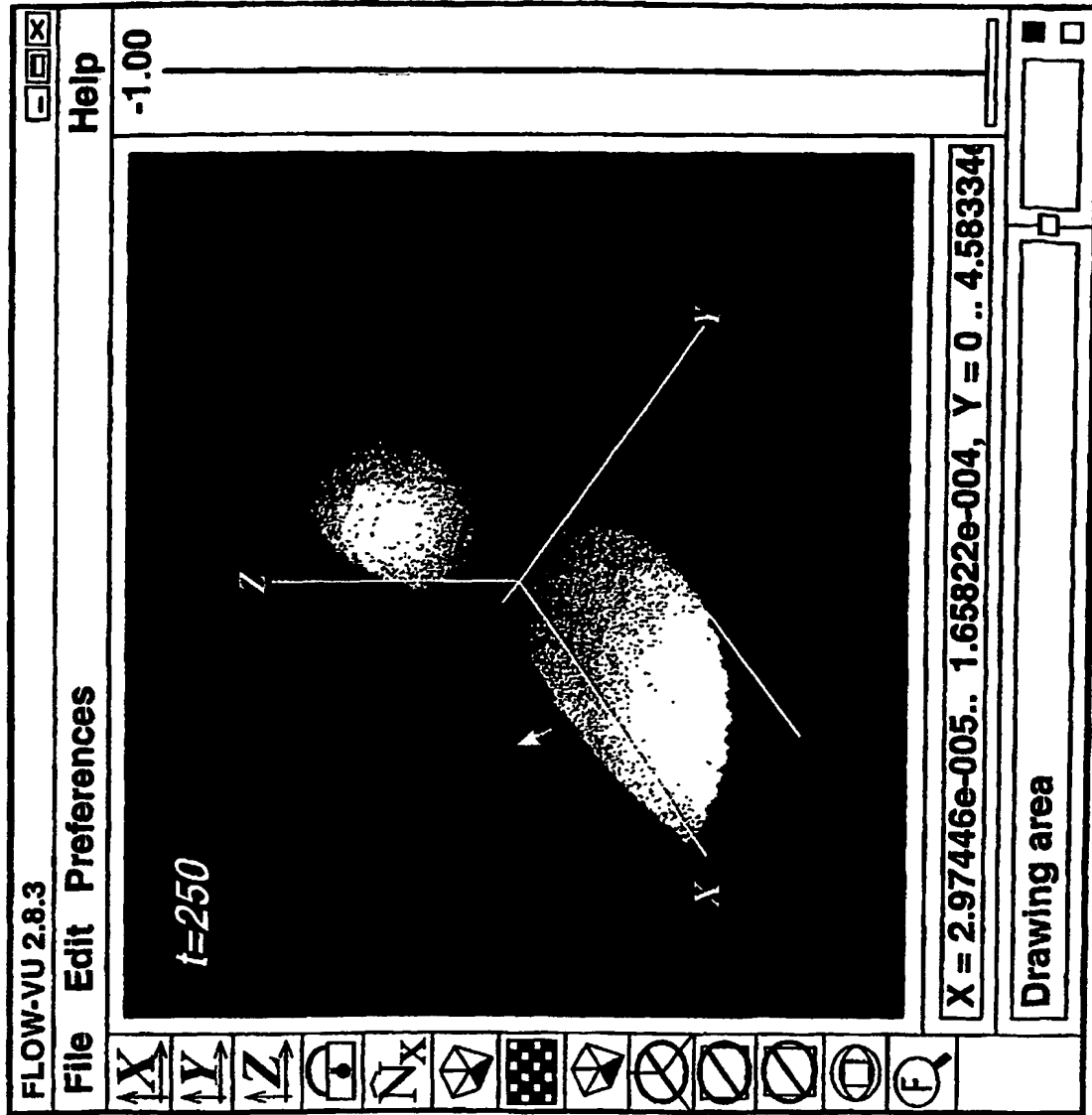
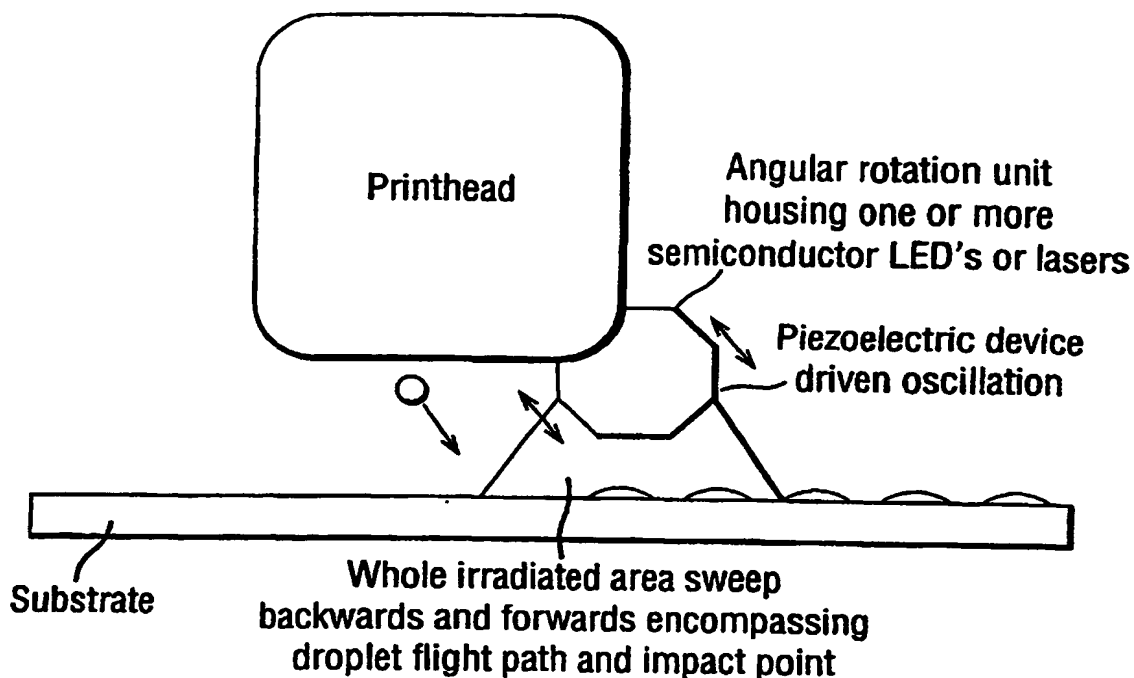
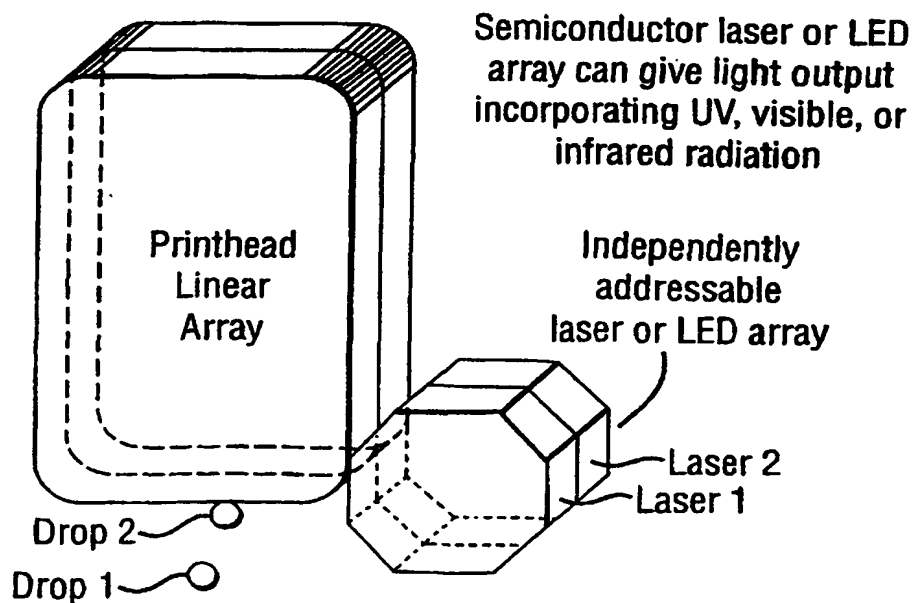


FIG. 6

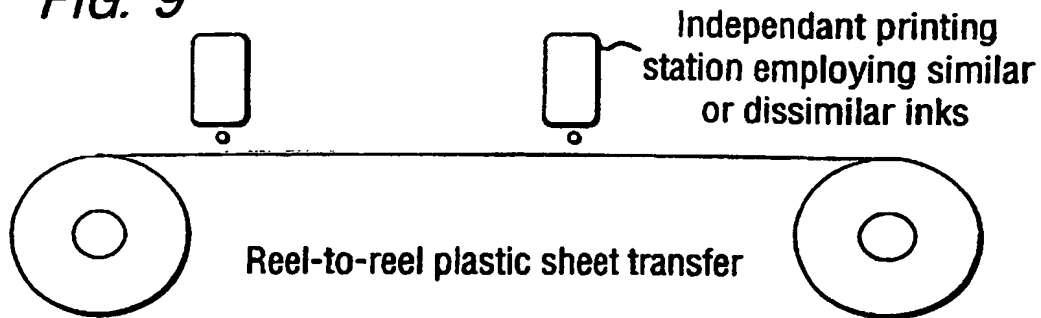
**FIG. 7**



**FIG. 8**

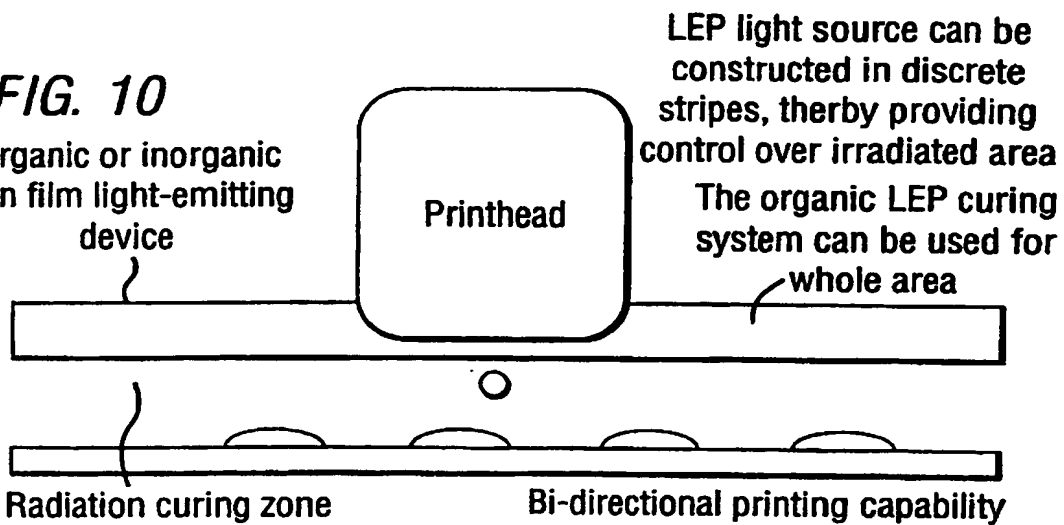


**FIG. 9**



**FIG. 10**

Organic or inorganic thin film light-emitting device



**FIG. 11**

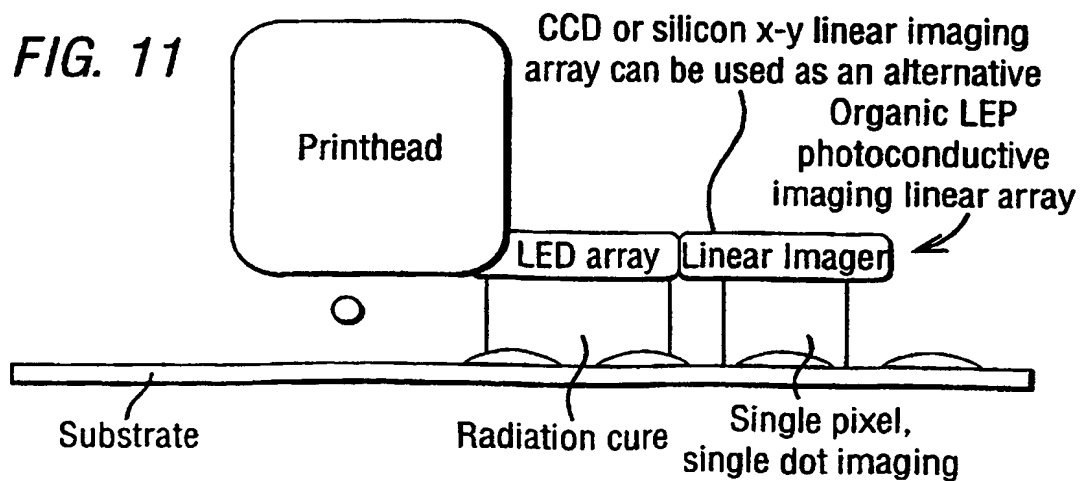




FIG. 12

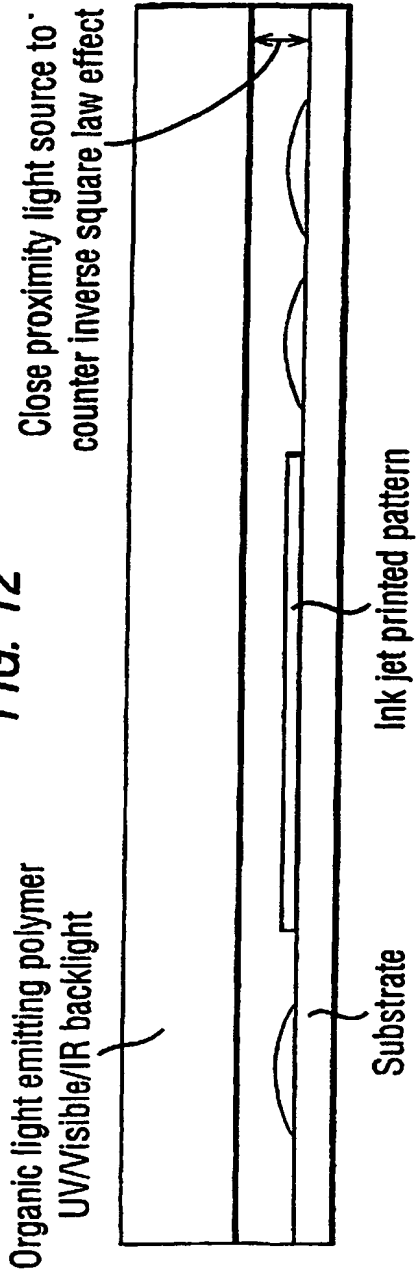


FIG. 13

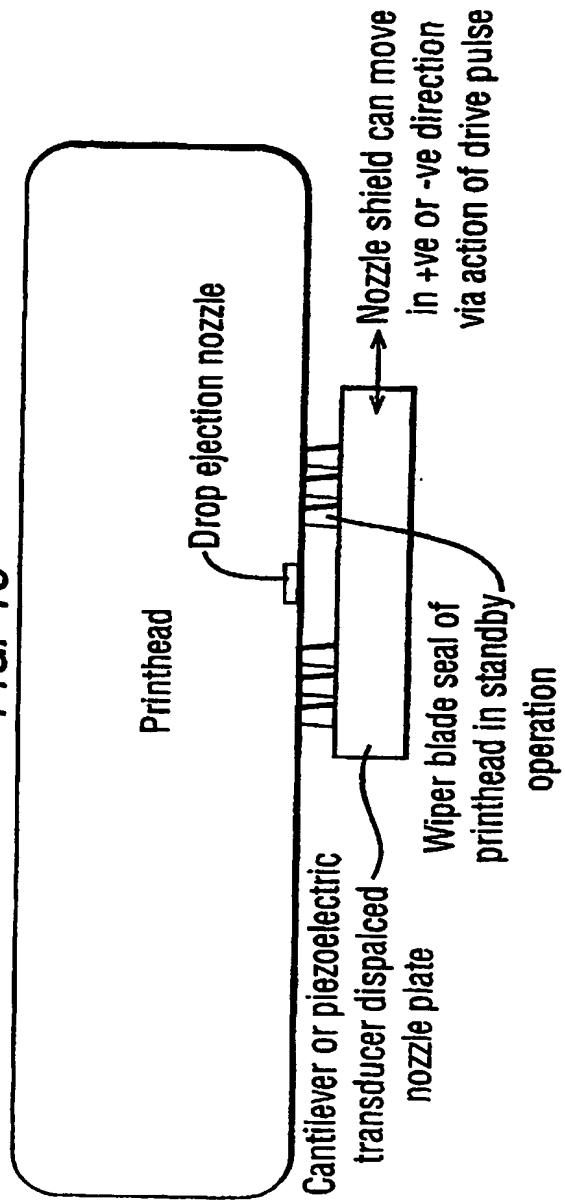


FIG. 14

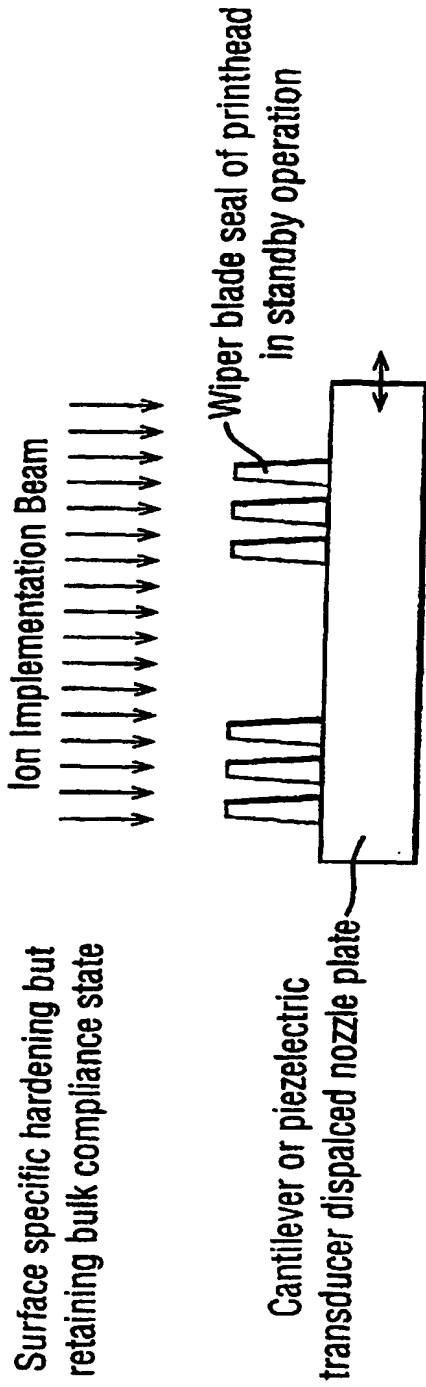
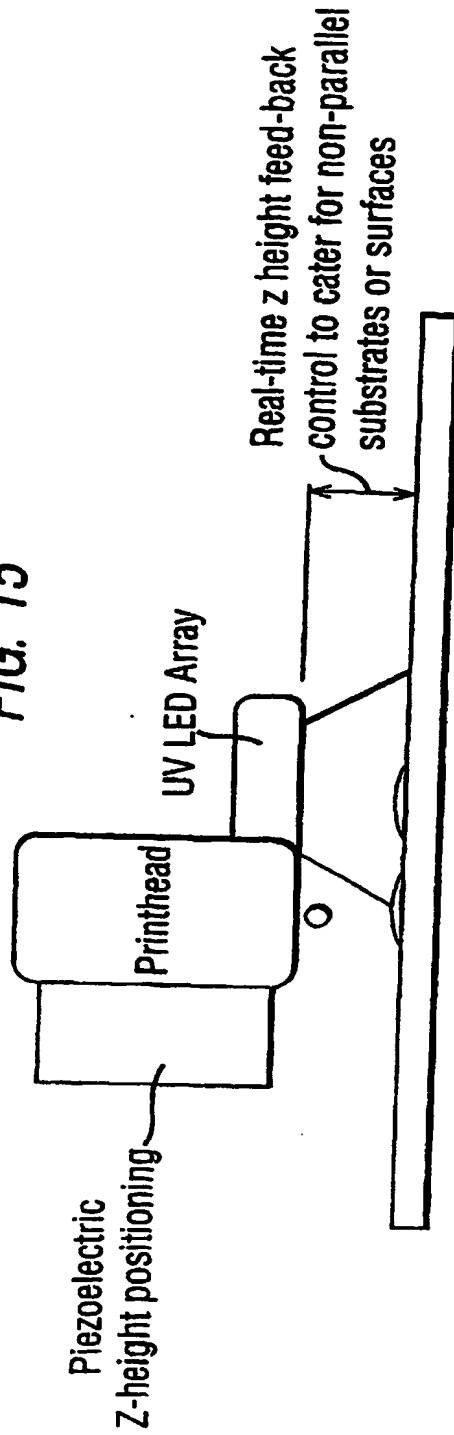
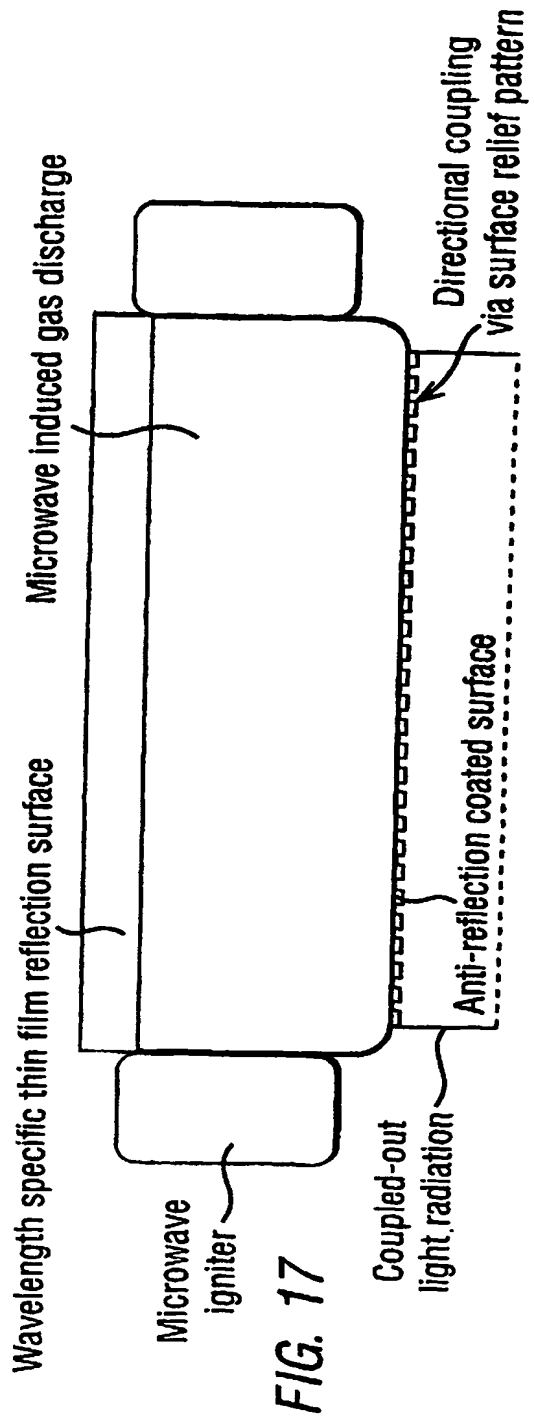
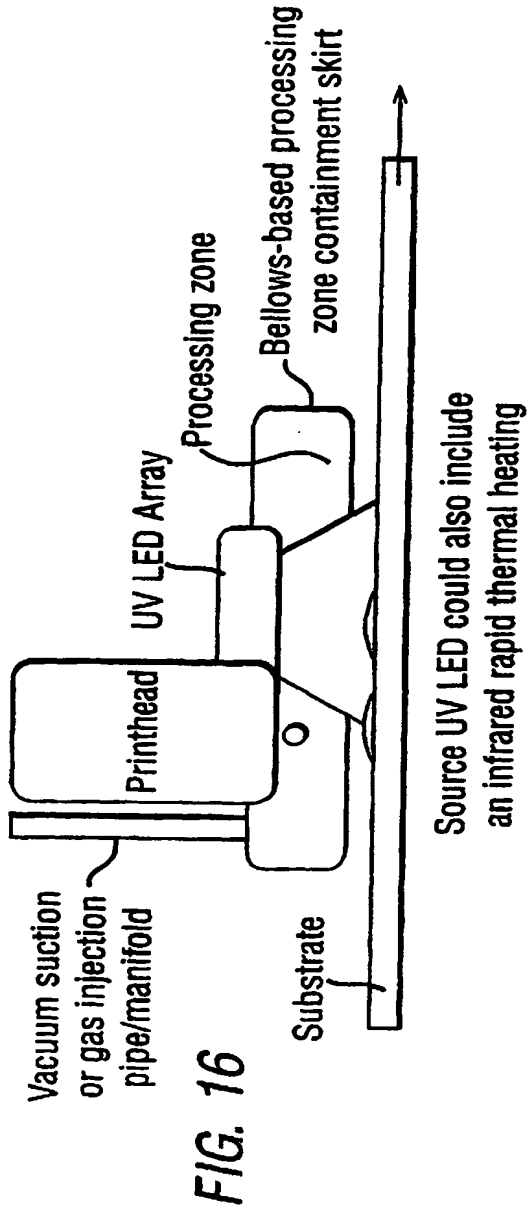
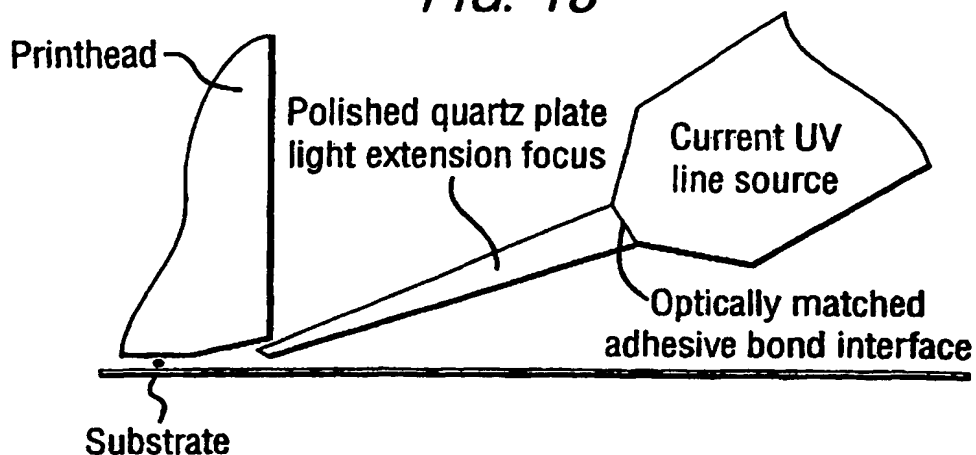


FIG. 15

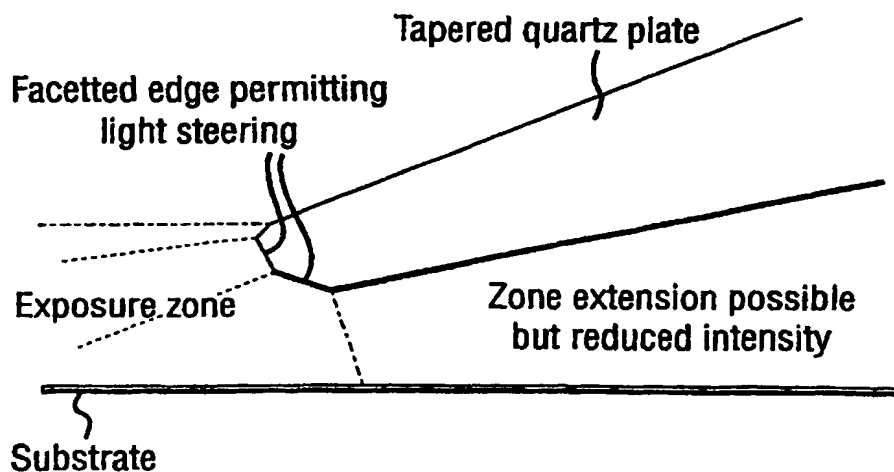




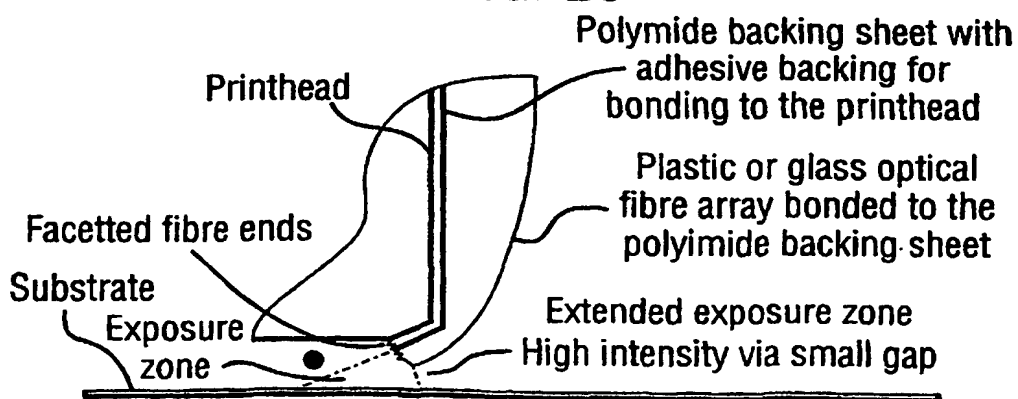
**FIG. 18**



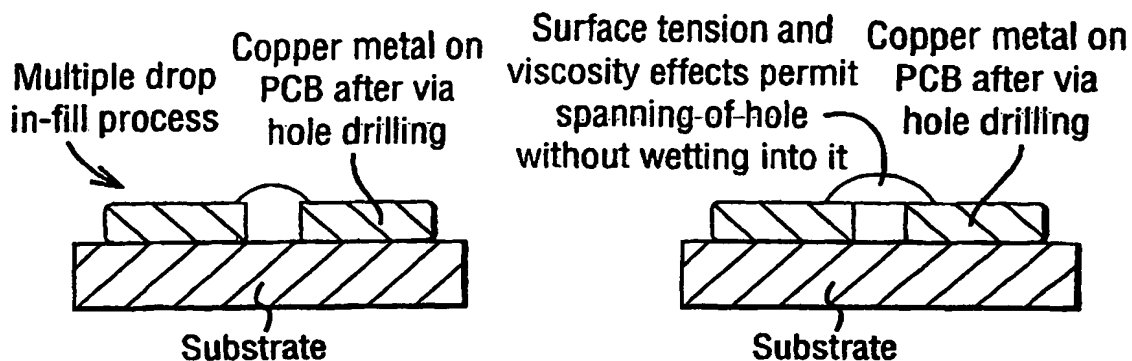
**FIG. 19**



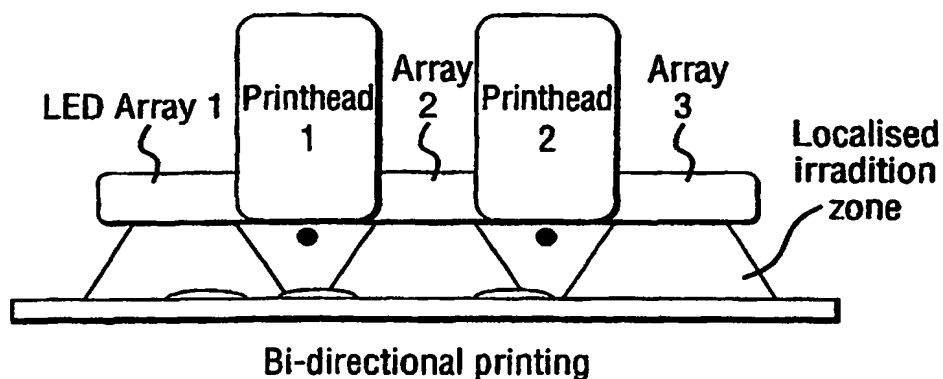
**FIG. 20**



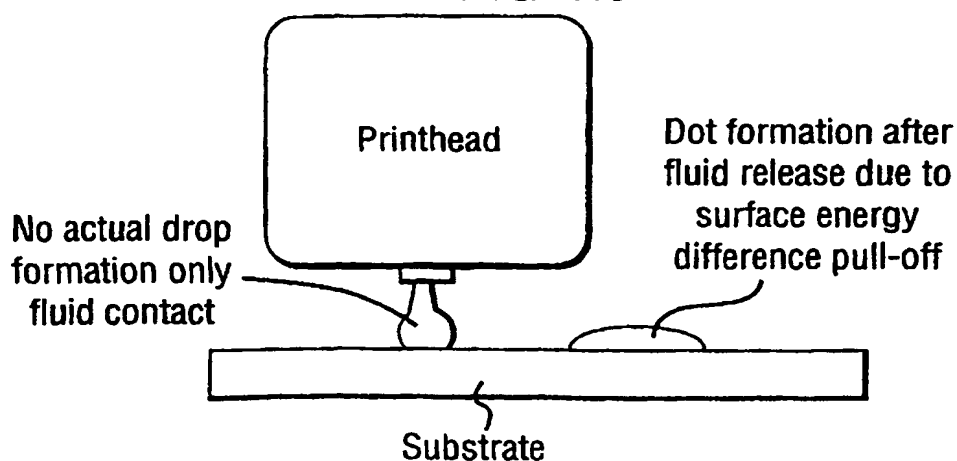
**FIG. 21**



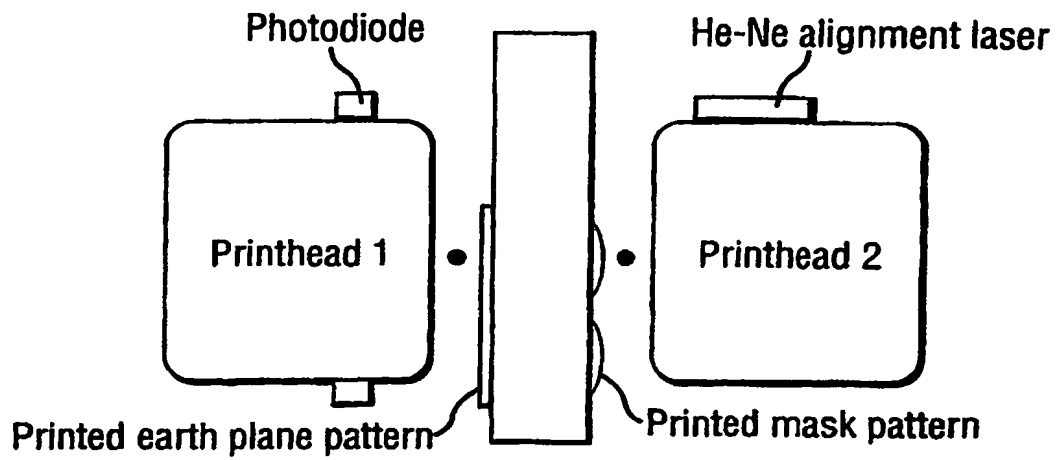
**FIG. 22**



**FIG. 23**



**FIG. 24**



**FIG. 25**

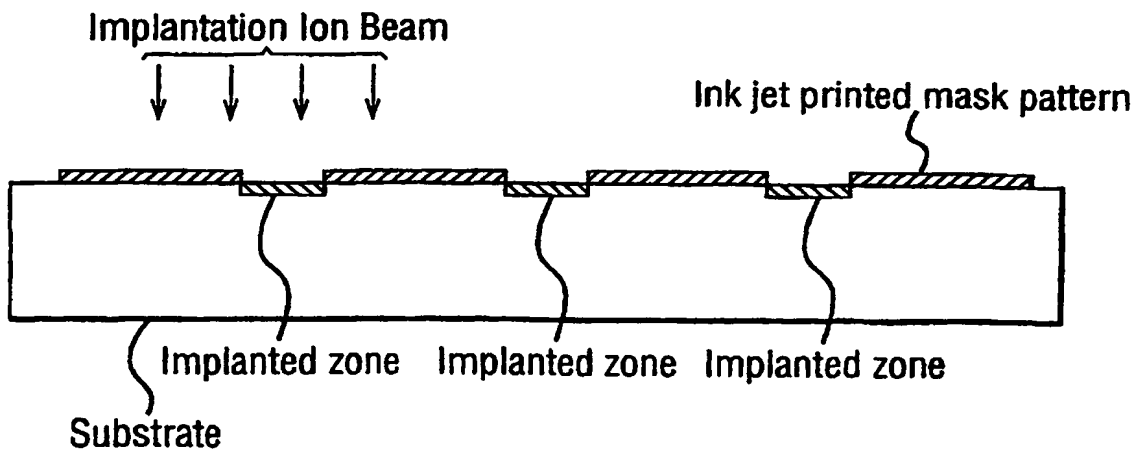


FIG. 26

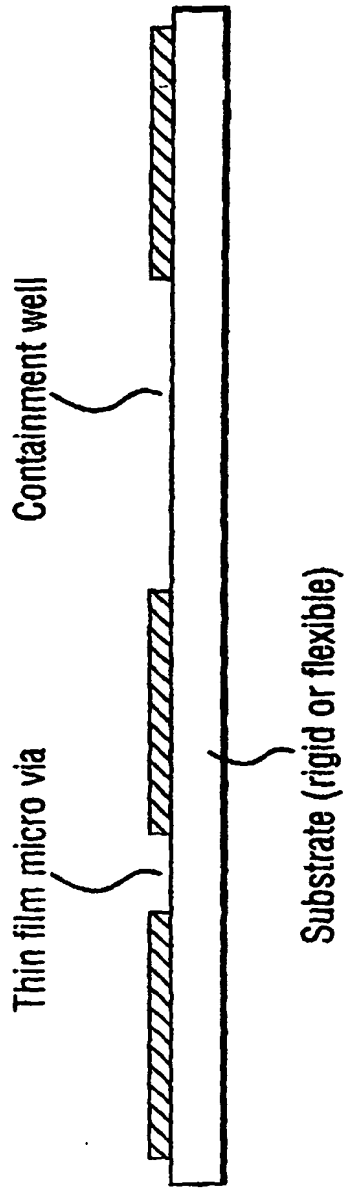
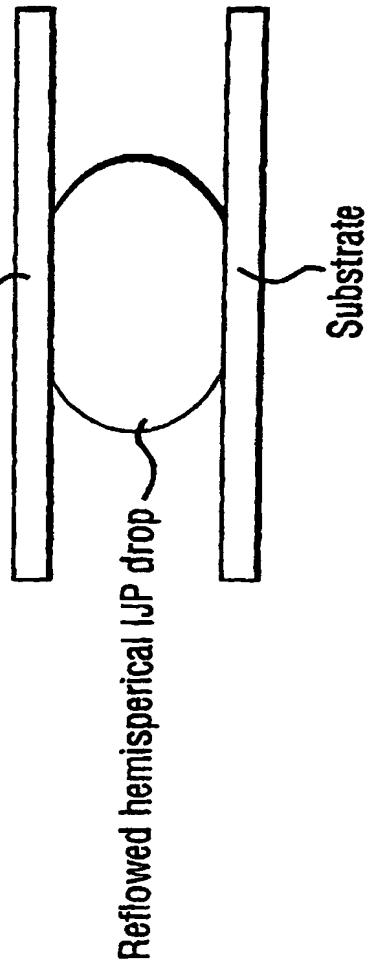


FIG. 27

Auto-alignment of two pieces  
via spacer surface tension



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**